Environmental Chemistry for a Sustainable World

Eldon R. Rene
Erkan Sahinkaya
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Sustainable Heavy Metal Remediation

Volume 2: Case studies

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Editors
Eldon R. Rene
UNESCO-IHE Institute
for Water Education
Delft, The Netherlands

Alison Lewis
Faculty of EBE
University of Cape Town
Cape Town, South Africa

Erkan Sahinkaya
Bioengineering Department
Istanbul Medeniyet University
Istanbul, Turkey

Piet N.L. Lens
UNESCO-IHE Institute for Water Education
Delft, The Netherlands

Department of Chemistry and Bioengineering
Tampere University of Technology
Tampere, Finland

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Preface

> Let us be good stewards of the earth we inherited. All of us have to share the earth's fragile ecosystems and precious resources and each of us has a role to play in preserving them. If we are to go on living together on this earth, we must all be responsible for it. (Kofi Atta Annan)

> Learning gives creativity, creativity leads to thinking, thinking provides knowledge and knowledge makes you great. (A. P. J. Abdul Kalam)

There is an unprecedented global demand for metals and other valuable resources due to surge in demand for technology, the increasing rate of technology development and the expansion of developing economies. At the same time, the growing global waste streams generated by this demand are becoming increasingly problematic. These waste streams include electronic waste, wastewaters from diverse industrial and mining activities, construction and demolition debris, metallurgical slags from smelting operations, industrial sludges, dusts and residues from metal extraction and refining, spent catalysts as well as many others (Fig. 1).

Paradoxically, the source of problems can also be the locus of the solution. The source of waste is often the source of the expertise to recover the valuable recyclable materials from complex products that have reached their end of useful lives. Although several metal removal technologies based on physical, chemical and biological processes have been successfully implemented in full-scale operation, metal recovery from wastes, which is beneficial for economic and environmental reasons, is still limited due to challenges arising from downstream processing. For instance, bioleaching of metals from their ores is a well-established technology with a number of full-scale applications. Conversely, bioleaching of electronic wastes to recover metals, which is a highly promising technology with low environmental impact and high cost-effectiveness, is a technology that is still in its infancy.

This book presents sustainable technologies for heavy metal removal and recovery from mining and metallurgical wastes, construction and demolition wastes, spent catalysts and electronic wastes (Fig. 2).

Fig. 1 Representative image of construction and demolition waste and waste generated from copper smelter operation

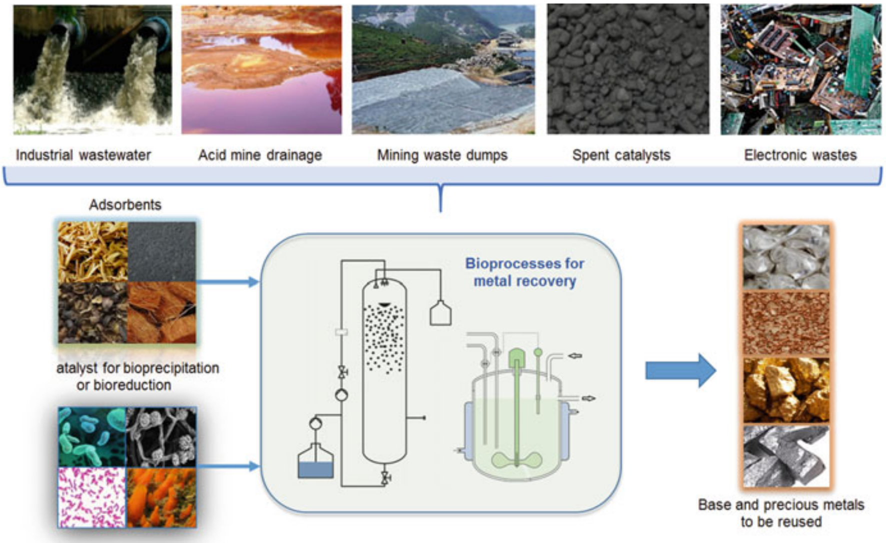

Fig. 2 Application of bioprocesses for the removal and recovery of heavy metals from different contaminated sites. The treated water can be used for the recovery of base and precious metals that can be reused

In Chap. 1, the focus is on life cycle assessment (LCA), which is a method that can be used to evaluate the suitability of various technologies. LCA is applied to a bioleaching process to recover metal from electronic waste, an increasingly significant waste stream. Adsorption technology as described in Chap. 2 can also be used for the removal of metals from contaminated waste streams and other liquid and gas phase toxic pollutants. A wide range of adsorbents, including chitosan, fly ash, used rubber tyre, wood char, rice husk and alumina silicates, have been evaluated for the removal of heavy metals from water. These can be effective and economical, as well as environmentally friendly, as they can be derived from renewable resources.

Metal recovery from industrial and mining wastewaters can also be performed using sulphate-reducing bioreactors as described in Chap. 3. Various substrate options, i.e. the carbon source, and bioreactor configurations are available. However, metal recovery is hampered because metals precipitate partly in the biomass. There is future potential to explore the efficient use of substrates and intelligent control of process conditions for the recovery of metals in bioreactors. Biological sulphate reduction can also be used for the treatment of construction and demolition debris (Chap. 4). This debris contains high metal and sulphate concentrations, which can create environmental problems due to odours and health impacts due to hydrogen sulphide gas generation, especially at landfill sites. In order to reuse this debris, both sulphate and heavy metals have to be removed. Both chemical and biological processes can be used. Although chemical sulphate removal processes perform well, chemicals such as barium and lead compounds have to be added. Biological sulphate reduction is an environmentally friendly and sustainable option. Metals are precipitated as metal sulphides, and excess sulphide can be recovered as elemental sulphur or sulphuric acid.

In Chap. 5, another important aspect of metal remediation that is related to lead and zinc metallurgical slag mineralogy and weathering is discussed. Predicting the environmental impact requires an understanding of minerals at microscopic scales as well as mineral-water interactions. This requires detailed characterisation of slag mineralogy and surface area, as well as performing dissolution tests. However, the usual short-term tests do not have the capacity to predict tens to hundreds of years of reactivity of these metallurgical wastes. From the view point of recovering base metals from metallurgical slags, it is recommended to manipulate and combine conditions for both chemical and biological leaching for successful heterotrophic leaching of metals.

Two other important environmental issues, such as the growing demand for metals and environmental impacts caused by metallurgical wastes, have been addressed in Chap. 6 with a focus on the extraction and recovery of heavy metals. Wastes from ferrous and non-ferrous metallic industries are a potentially important resource for metal extraction. Sludges, dusts and other wastes generated by metallurgical industries still contain significant amounts of valuable base and heavy metals, precious metals like gold and silver as well as rare earth elements, depending on the nature of the mining site and composition of primary ores used. It is possible to use various hydrometallurgical and bio-hydrometallurgical leaching processes for the extraction of metals from these wastes. A combination of knowledge on the mineralogical composition of waste with various leaching and metal recovery processes will help to use these metallurgical wastes as potential secondary sources of metals.

In Chap. 7, a similar case study is presented in the form of recovery of molybdenum from spent catalysts, since spent catalysts are generated in large quantities as solid waste on a yearly basis. Consequently, from both an ecological and an economical viewpoint, metal recovery from spent catalysts is very important. It is possible to recover molybdenum using chemical leaching, which offers yields exceeding 90%. Although bioleaching offers a more cost-efficient, simpler and more environmentally friendly process, it has long leaching cycles of approximately 20 days and low extraction efficiencies of molybdenum.

In Chap. 8, recovery of metals from electronic waste, the fastest-growing segment of solid waste, has been presented as an important secondary source of metals. Copper is the predominant metal by weight, along with substantial amounts of other base metals and precious metals. Therefore, the composition of leachate solutions from electronic waste is very complex, and thus novel strategies are required. Biotechnological metal recovery techniques enable environmentally friendly and cost-effective processes and are expected to play a significant role in sustainable development.

With individual chapters of this book focussing on applications and limitations of different technologies, it is intended that this book will serve as a useful resource for chemical engineers, environmental engineers, mining engineers, biotechnologists, graduate students and researchers in these areas. We also hope that by illustrating increasing numbers of case studies of metal removal and recovery from complex wastes, the expertise and knowledge necessary for sustainable metal remediation will be developed and enhanced. Ultimately, we hope to see engineers, chemists and biotechnologists playing leading roles in realising the full cycle of metal extraction, refining and, finally, recycling and recovery.

We wish to express our appreciation to the multidisciplinary team of authors for discussion and communications and above all for their scientific contribution to this book. We are very grateful to Prof. Eric Lichtfouse (French National Institute for Agricultural Research, INRA, France) for providing many perceptive editorial comments and accepting this book to be a part of the book series on *Environmental Chemistry for a Sustainable World*. Thanks to Ms. Judith Terpos from Springer (the Netherlands) and her production team for supporting us constantly during the editorial process. We firmly believe that the information contained in this book will enhance the skills of the readers, while it will also deepen their fundamental knowledge on resource recovery from wastes.

We hope you like reading this book.

Delft, The Netherlands	Eldon R. Rene
Istanbul, Turkey	Erkan Sahinkaya
Cape Town, South Africa	Alison Lewis
Delft, The Netherlands	Piet N.L. Lens

Contents

Contributors

Ansar Anjum Department of Applied Science and Humanities, Galgotias College of Engineering and Technology, Greater Noida, India

Francois Bordas Université de Limoges, Groupement de Recherche Eau-Sol-Environnement (GRESE), Faculté des Sciences & Techniques, Limoges, France

Luiz H. A. Figueiredo Universidade Estadual de Montes Claros, Solos e nutrição de plantas, Janauba, MG Brazil

Denys Kristalia Villa Gómez School of Civil Engineering, University of Queensland, St Lucia, QLD, Australia

Gilles Guibaud Université de Limoges, Groupement de Recherche Eau-Sol-Environnement (GRESE), Faculté des Sciences & Techniques, Limoges, France

Heinrich A. Horn Universidade Federal de Minas Gerais, NGqA-CPMTC, Instituto de Geociências, Belo Horizonte, MG, Brazil

Arda Işıldar Université Paris-Est, Laboratoire Geomatériaux et Environnement (LGE), Marne-la-Vallée, France

UNESCO-IHE Institute for Water Education, Delft, The Netherlands

Pimluck Kijjanapanich UNESCO-IHE Institute for Water Education, Delft, The Netherlands

Department of Environmental Engineering, Faculty of Engineering, Chiang Mai University, Chiang Mai Thailand

Piet N.L. Lens UNESCO-IHE Institute for Water Education, Delft, The Netherlands

Department of Chemistry and Bioengineering, Tampere University of Technology, Tampere, Finland

Eldon R. Rene UNESCO-IHE Institute for Water Education, Delft, The Netherlands

Manivannan Sethurajan Université Paris-Est, Laboratoire Géomatériaux et Environnement (LGE), EA 4508, UPEM, Marne-la-Vallée, France

UNESCO-IHE Institute for Water Education, Delft, The Netherlands

Yann Sivry Institut de Physique du Globe de Paris, Sorbonne Paris Cité, Univ. Paris Diderot, UMR 7154, CNRS, Paris, France

Eric D. van Hullebusch Université Paris-Est, Laboratoire Géomatériaux et Environnement (LGE), EA 4508, UPEM, Marne-la-Vallée, France

UNESCO-IHE Institute for Water Education, Delft, The Netherlands

Jack van de Vossenberg UNESCO-IHE Institute for Water Education, Delft, The Netherlands

Mirjana Vemic Université Paris-Est, Laboratoire Géomatériaux et Environnement (LGE), EA 4508, UPEM, Marne-la-Vallée, France

Marco Villares Architect and Industrial Ecologist, Delft, The Netherlands

Nang-Htay Yin Université Paris-Est, Laboratoire Géomatériaux et Environnement (EA 4508), UPEM, Marne-la-Vallée cedex 2, France

Chapter 1
Life-Cycle Assessment of Metal Recovery from Electronic Waste

Marco Villares

Abstract Increasing technological development is driving the demand for metals, especially in the field of electronics. Conversely, electronic waste is a growing global waste stream which is becoming more problematic in its management. Unsafe disposal contributes to environmental pollution as well as wasting secondary resources and threatening human health, particularly in developing countries with immature waste treatment and recycling technologies. This chapter gives an outline of European regulations and an overview of the global electronic waste situation and formal and informal recycling in the developed and developing countries. Since metal concentrations in electronic waste can be even higher than in mineral ores and some metals are considered critical in supply, there is a strong incentive to recover them as a secondary resource.

Life-cycle assessment, LCA, is an analytical tool based on physical metrics of material and energy flows of the life-cycle of a product or service system used to evaluate its environmental performance. The recovery of valuable metals from electronic waste can be achieved by bioleaching, involving microorganisms working at near ambient temperatures. The possible environmental performance from a life-cycle perspective of this novel metal recovery technique is evaluated in a summarised illustrative case study applying life-cycle assessment.

Keywords Electronic waste • Life-cycle assessment • Circular economy • Metal recovery • Bioleaching • Scenario • LCA • Recycling • Secondary resource

Contents

M. Villares (✉)
Architect and Industrial Ecologist, Delft, The Netherlands
e-mail: m.villares@umail.leidenuniv.nl

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1.1 Introduction

Our contemporary technological civilisation requires the diverse use of many sorts of metals in order to operate. Huge quantities of bulk metals such as steel, copper and aluminium are used to produce buildings, electrical wires and aircraft respectively. With increasing economic and technological development, the unique properties of every metal have been applied to improve product performance (Reck and Graedel 2012). There is more demand for other types of metals, such as rare earth metals. These are used in novel technologies and to produce the generators and batteries for renewable transport and energy systems. For example, thin film solar cells, which are cheaper to make than single crystal silicon, need indium, gallium, selenium and tellurium, while the large magnets used in wind turbines generators require neodymium, praseodymium and dysprosium to improve their resistance to overheating (Bradshaw et al. 2013). Moreover, a shift to renewable energy systems could be far more resource intensive than the present, fossil-fuel-based system (Kleijn and Van der Voet 2010; Kleijn 2011).

With the drive for cleaner technologies, the use of more electronic information technology and the development of emerging economies, demand for all metals is on the rise. At the same time, primary extraction can rely less on high-grade easily recoverable metal ores. Moreover, mining entails environmental risks owing to the toxic chemicals involved and it is energy intensive.

Large-scale inefficient use of metals over their whole life-cycle from extraction to disposal increases metals dispersed in the environment as pollutants that disrupt the biological functions of living organisms. Metals are considered strong contributors to ecotoxic impacts as they do not degrade in the environment and in principle their presence is for ever (Van der Voet 2013). Geopolitics and concerns regarding reliable, sustainable and undistorted access to certain raw materials is of growing concern within the European Union and across the globe (European Commission 2014a).

All the above factors underline the importance of utilising sources of metals in discarded products and other waste streams. These factors in turn provide the rationale for the development of more effective and efficient techniques for recycling and metal recovery. Within the landscape sketched above, waste electrical and electronic equipment plays a significant role as a growing waste stream and carrier of diverse secondary metals. In the following sections an overview of the electronic waste topic and management and recovery techniques for the metals it contains will be given. Then the life-cycle assessment (LCA) framework will be described before presenting the summary of a case study of its application to evaluate the environmental performance of bioleaching of electronic waste for copper recovery.

1.2 Electronic Waste and Metal Recovery

1.2.1 The Growth of Electronic Waste

In the developed and developing world, rising levels of wealth coupled with shortened product life-cycles driven by fast innovation and fashion have led to a dramatic rise in the global consumption of consumer goods (Kiddee et al. 2013; Breivik et al. 2014). Economies of scale have brought down the costs of electrical and electronic equipment and made it almost accessible for all in recent decades. The total number of discarded computers and other devices that generate electronic waste strongly correlates with a country's gross domestic product (GDP), since electrical and electronic items are now required for most contemporary economies to function (Robinson 2009).

Global amounts of electronic waste are already enormous, estimated to be between 20 and 50 million tonnes per year (Ongondo et al. 2011; Baldé et al. 2015). This comes to 3–7 kg/person each year, taking the world population to be 7 billion people. In Europe alone about 12 million tonnes of waste electrical and electronic equipment (WEEE) per year are generated, with an expected increase in the coming decades at a rate of at least 4% per year (Reuter 2013). At this rate, and assuming a European population of 500 million, an average of more than 30 kg/person per year in 2020 will be generated.

This growth is taking place throughout the present linear throughput economy, based on the steps of extraction, production, distribution, consumption and disposal. This mode of operation has two important consequences. First, increased exploitation of natural resources takes place (mining of finite minerals) with more potential of future scarcity (Graedel et al. 2015). Second, the generation of larger waste streams, which have been initially dispersed in the natural environment. Such waste electrical and electronic equipment has typically gone to local landfill sites or been exported for disposal to less-developed nations with less-stringent environmental regulations.

1.2.2 Disposal of Electronic Waste

Safe disposal of electronic waste is a challenge owing to the composition of the products, typically made up of heavy metals and other chemical components threatening to human health and the environment. Electronic waste can contain more than one thousand different substances, many of them toxic, such as arsenic, cadmium, hexavalent chromium, lead, mercury, selenium, and flame retardants that create dioxins emissions when burned (Widmer et al. 2005). Research has shown that toxic metals as well as polyhalogenated organic compounds such as polychlorinated biphenyls and polybrominated diphenyl ethers can be released from e-waste in landfills (Kiddee et al. 2013).

Within electronic waste, printed circuit boards have a heterogeneous, diverse and variable composition reflecting a market with different manufacturers and varying product designs according to their application (Hall and Williams 2007). Continuing advances in functional efficiency also result in more recent products being composed of fewer but more diverse materials (Reuter 2013). Hazardous materials derive from both the non-metallic and the metallic fraction of printed circuit boards. Although many brominated flame retardants used in the polymers of printed circuit boards are toxic, and halogen-free alternatives based on phosphate or metallic compounds are viable alternatives, the application of the former is still prevalent (Hadi et al. 2015). Many of these flame retardants are persistent, dissolve readily in organic fats and have been shown to reach high residue levels in sediments or bioaccumulate in living organisms (Li and Zeng 2012). Their ultimate behaviour and fate in water and soils will depend on how the materials are treated and to what degree dispersal in the environment takes place. In the metallic fraction of printed circuit boards, lead from the soldering tin is the most toxic fraction because of its higher concentration levels. However, mercury can also be present in switches and cadmium in the pins.

1.2.3 Electronic Waste Regulations in the European Union

The disposal issue has been addressed in part by wealthier nations by focusing on more environmentally benign end-of-life options for these products such as reuse, repair, refurbishment and recycling. Switzerland has been at the forefront of collection and recycling experiences with voluntary schemes in place even before the introduction of legislation (Ongondo et al. 2011).

Some legislation at the European Union level now regulates these issues restricting the use of hazardous substances, and requiring manufacturers to take back their products, recycle them and dispose of them safely. These are the respective directives restricting the use of hazardous substances (RoHS 2 Directive 2011/65/EU) and waste electrical and electronic equipment (WEEE directive 2012/19/EU) (Ongondo et al. 2011). Member states have to directly incorporate regulations into their national legal frameworks. The directives allow each member state room for interpretation in their implementation. Legislation stems from a general policy objective to reduce waste, preferably by prevention, and its promotion as a secondary resource for reuse or recycling.

1.2.3.1 Waste Electrical and Electronic Equipment Directive

This directive seeks to prevent and minimise electronic waste by reuse, recycling and recovery. A chief role is given to manufacturers and distributors being required to cover the costs of collection, treatment, recycling and recovery of electronic waste. Producers are required to set up individual or collective schemes which will finance the collection and treatment of electronic waste using the best available methods.

1.2.3.2 Restriction of Hazardous Substances Directive

This directive falls within the broader waste electrical and electronic equipment directive and is stricter, as its objectives are to protect human/animal health and to ensure the environmentally sound recovery and disposal of electronic waste (Stewart 2012). The onus again is on manufacturers as, since July 2006, in principle no electrical and electronic equipment and spare parts on the European Union market can contain six major toxic substances. These are lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls or polybrominated diphenyl ether, with important implications for printed circuit board manufacture (Ravi 2012). However, the directive has some leeway and foresees exemptions and specifies maximum concentrations in materials and components. Manufacturers have to mark their products with the European Conformity "CE" marking, CE being an abbreviation of the French "Conformité Européenne", and formally declare that their products are compliant with the directive. Such obligations also apply to importers and distributors. This compels manufacturers to establish as much uniformity in their products as is feasible (Stewart 2012).

1.2.3.3 Registration, Evaluation, Authorisation and Restriction of Chemicals Regulations

This legislation is based on the precautionary principle and tasks industry to take its own responsibility for the safe use of chemicals. Manufacturers are required to make exposure scenarios for their manufacturing processes and for identified uses of the substances on their own or in a preparation and for all life-cycle stages resulting from these uses. Industry is expected to manage the risks and has the burden of proof that they are acting responsibly. The objective is to support competition within the chemicals industry, while also protecting human health and the environment (Van Leeuwen 2007).

Substances of which more than one tonne is made or imported are to be registered in a database to pool information to avoid unnecessary testing by industry. Downstream and upstream information provision on health and safety, environmental risks and measures for the management of risks between manufacturers, importers, distributors and customers is mandatory. Chemicals that are carcinogenic, mutagenic or reproductive toxic substances and persistent, bioaccumulative toxic substances require previous authorisation before being put on the market. These aspects are managed by the European Chemicals Agency to ensure consistency across the European Union (Stewart 2012).

This drive for harmonisation across the European Union through these regulations has been fragmentary in its implementation due to differences in technological progress and ultimate responsibilities residing with each member state. Nevertheless, the implications for electronic waste of these directives are key defining elements regarding pre-production, production, and post-production of electronic waste streams (Hadi et al. 2015). Such standardisation and formalisation can be regarded as positive for the prospect of metal recovery from electronic waste. For example, in Germany household electronic waste is managed under a formal collection system under the responsibility of public waste-management authorities and retailers. The United Kingdom has a distributor take-back scheme and a producer-compliance scheme in place. Elsewhere in the developed world, such as the United States, municipal waste services handle the electronic waste stream. Voluntary schemes are also found there as well as in Australia and Canada, while Japan uses collection via retailers.

1.2.4 Export and Informal Recycling of Electronic Waste

Formal recycling of electronic waste in developed countries uses a treatment chain applying four operational phases to target the diverse material fractions (Li and Zeng 2012; Ghosh et al. 2015; Hadi et al. 2015). Decontamination aims to separate as much as possible any hazardous components and fractions. Liberation involves dismantling and sorting the substances into more or less clean fractions. This depends on the design and the composition of the product and the degree of bonding of the target fractions. The recyclate is then made suitable for treatment during size reduction, termed comminution. Treatment then isolates the desired material fractions for recovery or disposal by means of chemical, metallurgical and thermal processes. However, effective reprocessing technology, which recovers the valuable materials with minimal environmental impact, is expensive (Robinson 2009).

Thus, part of the electronic waste is exported outside Europe, possibly under unethical conditions, for reuse/recycling under inadequate working and environmental conditions that also do not result in an effective recovery of the metals (Kiddee et al. 2013). Hence developing countries present a more distressing case, where regulations and cleaner methods of disposal are not in place. This raises ethical concerns of problem shifting when wealthy nations export their electronic waste to them. China and India are currently at the forefront of electronic waste treatment in unsafe conditions, followed by other African, Asian and Latin American developing countries where consumption of electronic goods is growing (Ongondo et al. 2011).

Informal recycling is quite specialised and provides an income for practitioners in dedicated workshops but it is inefficient and unsafe. Products are manually dismantled using cutting torches, hammers and chisels to break apart solder connections. More complex components are cooked on a coal or electrically heated plate to melt them, in some cases with little or no control over temperature and extraction of poisonous exhaust fumes. Much of the material is lost and workers and the environment are exposed to toxins (Ongondo et al. 2011; Li and Zeng 2012; Reuter 2013).

Contamination can happen locally in developing countries, but such problem shifting can rebound on the e-waste originators. Wealthy nations have a compelling incentive to deal with the issue, since electronic waste contaminants become omnipresent, being re-exported in food and manufactured products along global supply chains back to the developed world, constituting a global health risk (Robinson 2009).

Thus within the broader context of economic growth, increasing consumption and waste generation has resulted in circumstances that challenge the prevailing logic of business-as-usual practices. The global level of production and consumption creates large flows of both toxic and potentially valuable substances (Widmer et al. 2005). Large primary reserves of metals still exist, yet their extraction entails a high environmental burden compounded by declining ore grades of these reserves (Van der Voet 2013). Recycling can contribute to a solution by diminishing part of the increased demand for metals and the related energy and resource use for their production. Often potential ecological benefits of recycling are cancelled out if electronic waste has to be transported long distances, owing to the negative environmental effects of fossil-fuel-based transportation. However, the recycling process itself can have a lower ecological impact than landfilling of incinerated electronic waste (Robinson 2009). Recycling is one of the most immediate, tangible and low-cost investments available for decoupling economic growth from environmental degradation and escalating resource use (Reuter 2013).

1.2.5 The Circular Economy

These issues align with key aspects of the currently vaunted circular economy model (Ellen MacArthur Foundation 2013). Acknowledging the limits of linear consumption, this model proposes decoupling of the current unsustainable economy from material inputs. It also highlights potential economic opportunities arising from using resources more efficiently and effectively. Moreover, the precarious availability of primary resources exposes economies to risks of scarcity and rising costs of extraction. Benefits are to be gained from reducing waste at all points of the material chain and minimising disposal at end of life by reuse and recycling. Traditional concepts of use and ownership are questioned. The model largely foresees a partnership between consumers and producers where reusable materials are returned to the producers to close material loops. The European Union has recognised the multifaceted nature of the challenge to reform products, material and value chains, identify barriers in consumer habits, and develop new economic models and financial instruments to promote transition to a circular economy (European Commission 2014b).

1.2.6 Electronic Waste as a Secondary Metal Resource

Electronic waste has a heterogeneous, diverse and variable composition, reflecting a market with several manufacturers and product designs varying according to their application (Hall and Williams 2007). More recent products are composed of fewer but more diverse materials, reflecting advances in functional efficiency (Reuter 2013). Electronic waste has an average predominant metal content of about 60%, as illustrated in Fig. 1.1, comprising all the base, heavy and precious metals and rare earth metals. The most well-known precious metals, gold, silver, platinum and palladium, are less reactive and rarer than base metals and have high economic value. The rare earth metals are a group of 17 chemically similar metallic elements consisting of the 15 lanthanides, plus scandium and yttrium. Primary mining of rare earth metals is costly and complex because they occur associated with each other in varying ratios in minerals and ores (Binnemans et al. 2013).

Electrical and electronic equipment can sometimes contain up to 50 different kinds of metallic elements, as indicated in Table 1.1, sometimes in quite small amounts.

However, electronic waste streams have greater concentrations of metals than natural ores, which makes their recycling as secondary resources significant for both economic and environmental motivations (Zeng et al. 2012). For example, the printed circuit boards found in all electronic equipment typically contain the material concentrations shown in Table 1.2.

The demand for copper and zinc is anticipated to rise (Ilyas and Lee 2014a). Furthermore, rare earth metals and platinum group metals are subject to high supply risk, being critical raw materials for renewable energy production and batteries (Moss et al. 2013; European Commission 2014a, c). The major economic driver for e-waste recycling is the recovery of the precious metals, followed by copper and zinc (Lee and Pandey 2012). Therefore it is advantageous to implement effective methods to recover these useful secondary source metals to enhance resource utilisation instead of discarding them. However, adequate collection, sorting and

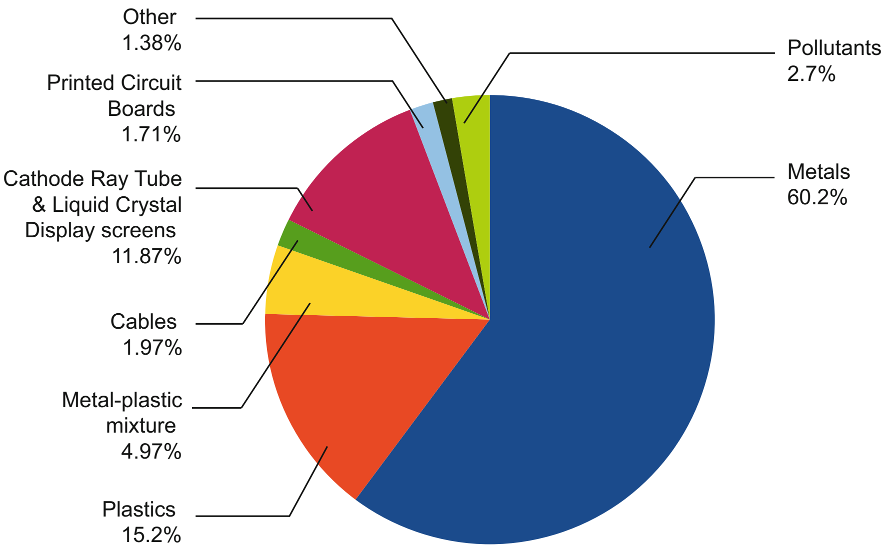

Fig. 1.1 Typical electronic waste material fractions (Adapted from Widmer et al. 2005), showing the proportionally high metal content of 60%

pre-processing and the long lifetimes of certain product groups of electronic waste pose a significant challenge for taking advantage of this dispersed secondary material source (Moss et al. 2013).

1.2.7 Metal Recovery Techniques

Traditional methods of extraction of metals from ores have been applied for thousands of years by mankind. Pyrometallurgy involves applying heat and high temperatures, while hydrometallurgy uses chemical solutions. Pyrometallurgical techniques apply roasting to convert compounds just below their melting points or smelting, which totally melts the ore into two liquid layers, one containing the metals and the other the waste rock. Hydrometallurgy involves the dissolving of compounds from an ore by an aqueous solvent otherwise known as leaching. In general, an oxidative leaching process is required for the extraction of the targeted base and precious metals. For example copper can be extracted using lixiviants such as sulphuric acid, aqua regia, which is a mixture of nitric acid and hydrochloric acid, ammonia, and hydrogen peroxide combined with acids (Tuncuk et al. 2012). Precious metals can be extracted using cyanide, aqua regia, thiourea and thiosulfate (Cui and Zhang 2008).

Further metal extraction can be done by electrowinning, where, after an electric current is passed through the solution, the metal ions are deposited onto an electrode

Table 1.1 Overview of the applications of metals in electrical and electronic equipment (Reuter 2013). The ubiquity and diversity of their applications is shown, highlighting the sensitivity to metal supply of these now indispensable products

Metal	Application in electrical and electronic equipment
Ferrous metal	Casings, as major element in magnets, magnetic coils
Aluminium	Casings, partly cables
Magnesium	Casings, body of cameras
Copper	Cables, connectors
Gold	Contacts, transistors, diodes, switches, transistors, integrated circuits
Palladium, platinum, rhodium	Capacitors, connectors, contacts, transistors, diodes, soldering
Silver	Lead-free soldering, capacitors, contacts, batteries, radio frequency identification chips, photovoltaic cells
Antimony	Alloying element, additive for flame retardants, soldering element, semi-conductor technology and photocells, additive in cathode ray tube glass
Gallium	Semiconductors, laser diodes, light emitting diodes, photo detectors, photovoltaic cells, integrated switches
Germanium	Photovoltaic cells, glass fibre, optical glasses glass fibre, semi-conductive chips
Indium	Flat panel screens, thin-film-photovoltaic cells, semi- conductors, light emitting diodes
Cobalt	Lithium-ion and nickel metal hydride batteries, magnets
Rare earth metals, neodymium, dysprosium, scandium, lanthanum and yttrium	Magnets, compact florescent bulbs, phosphors, fuel cells, nickel metal hydride batteries
Tantalum	Capacitors
Beryllium	Beryllium-copper-alloys, beryllium oxide-ceramics, metallic beryllium
Tellurium	Thin film photovoltaic cells, photoreceptors, photoelectrical devices
Tungsten	Tungsten carbide, electrodes, cables and electrical components, additives in cathode ray tube glass
Niobium	Niobium-steel alloys, super alloys magnets, capacitors
Tin	Lead-free soldering, liquid crystal displays, photovoltaic cells, miniaturized capacitors

(Charles et al. 2014). Other metal-extraction methods include adsorption on activated carbon, ion exchange, precipitation, cementation and solvent extraction, used in conjunction with electrowinning. The selected method depends on the leaching reagent system metal concentrations and the presence of impurities (Tuncuk et al. 2012).

Table 1.2 Comparison of typical copper and gold concentrations in natural ores and printed circuit boards (Erüst et al. 2013). The concentrations in electronic waste exceed by far those of mineral ores, providing a clear rationale for their recycling from this waste stream

Metal	Concentration in natural ore	Concentration in printed circuit boards	Magnitude increase of concentration in printed circuit boards
Copper, Cu	~5–10 kg/ton (~0.5–1%)	~200 kg/ton (~20%)	20 to 40-fold
Gold, Au	~1–10 g/ton (~0.0001–0.001%)	~250 g/ton (~0.025%)	25 to 250-fold

Some of these processes, such as pyrometallurgy, have been successfully applied to electronic waste to recover valuable metals by firms such as Umicore in Belgium and Outotec in South Korea (Van der Voet 2013). However, the nature of these traditional processes can have important environmental impacts. Their high-temperature furnaces generate polluting chemicals, such as dioxins, and are energy intensive.

Biohydrometallurgy, a potentially more environmentally friendly alternative, involves using microbes with the natural capability to extract metals for their own metabolic functions. Certain strains of microorganism, such as bacteria, archaea and fungi, can survive in environments with high metal concentrations, whereby the metals are leached to solution after using them as an energy source (Mishra and Rhee 2014). For example, acidophilic iron and sulphur oxidizing bacteria can directly and indirectly extract bivalent metals to solution (Cui and Zhang 2008; Petersen 2010; Erüst et al. 2013). Heterotrophic bacteria that require an organic carbon source for growth, such as *Pseudonomonas putida*, produce cyanide, which can be used to extract precious metals (Işıldar et al. 2015). The microorganisms suitable for metal bioleaching with respect to electronic waste still remain inadequately characterised and limited literature exists on their possible mode of interaction and extent of leaching (Ilyas and Lee 2014a). To optimise biohydrometallurgical processes, important parameters need to be controlled, such as pH, temperature, growth media composition, oxygen and carbon dioxide content (Watling 2006). Other parameters such as toxic elements present in the electronic waste and acid/base consumption are also relevant (Erüst et al. 2013). Current investigations to optimise applications of bioleaching for metal recovery from electronic waste are in their early stages at the level of laboratory studies, mainly using shake flasks. The process purportedly has potential to afford environmental benignity, operational flexibility, and lower costs with less energy consumption than the traditional methods (Ilyas and Lee 2014b). An early assessment of its potential environmental performance from a life-cycle perspective can provide insights for further development.

1.3 Life-Cycle Assessment

A tool for the evaluation of the environmental impacts of a technology is life-cycle assessment. It has its origins in energy analysis, which led to the first chiefly comparative life-cycle studies of consumer products in the 1960s and 1970s. Since these first studies on diapers and drink containers, the methodology has been further developed, standardised (International Organisation for Standardization (ISO) 2006) and applied to assess a wide range of services and products such as waste incineration, building materials, military systems, and tourism (Guinée et al. 2011).

1.3.1 Life-Cycle Assessment Methodology

Life-cycle assessment is a comprehensive analytical tool based on physical metrics of material and energy flows of the life-cycle of a product or service system, principally applied to improve sustainability performance (Rebitzer et al. 2004; International Organisation for Standardization (ISO) 2006). The boundary of analysis is typically from cradle to grave, taking into account extraction, production, distribution, consumption and disposal. All upstream and downstream processes should be considered, aiming to identify their related potential environmental burdens and avoid problem shifting between life-cycle phases, between regions or between environmental problems (Guinée et al. 2002; Finnveden et al. 2009). It goes beyond the typical sole focus on a production site and the specific manufacturing process or processes involved there (Castro-Molinare et al. 2014).

The method assumes that the product system is in a steady state to quantify its associated environmental interventions and their impacts. These impacts can be climate change, acidification, eutrophication, stratospheric ozone depletion and resource depletion, and/or others chosen, depending on the application. Other types of impacts of financial, political, social or other nature are not dealt with by the methodology (Guinée and Heijungs 2005). Apart from the identification of processes where environmental performance can be improved, known as hotspots, Fig. 1.2 shows that LCA can also be applied for product development, strategic planning, policy making and marketing (Guinée et al. 2002).

The product or service system is composed of unit processes, connected by material, energy, product, waste and service flows shown in Fig. 1.3. It is in turn embedded in an economic subsystem that is made up of the following main activities: mining of raw materials; production of materials, products and energy; use and maintenance of products; waste treatment and processing of discarded products; and transport (Udo de Haes and Heijungs 2009).

The product system can be considered as two subsystems, a foreground system governed by internal factors and a background system by external ones. The foreground system includes those processes “whose selection or mode of operation

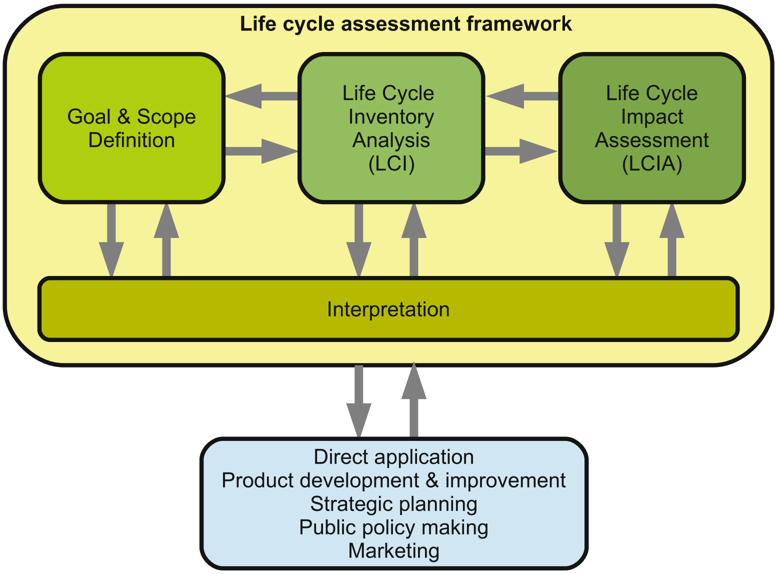

Fig. 1.2 Life-cycle-assessment-framework diagram showing the four phases of goal and scope definition, life-cycle inventory analysis, life-cycle impact assessment and interpretation, as well as possible applications of the method (Guinée and Heijungs 2005)

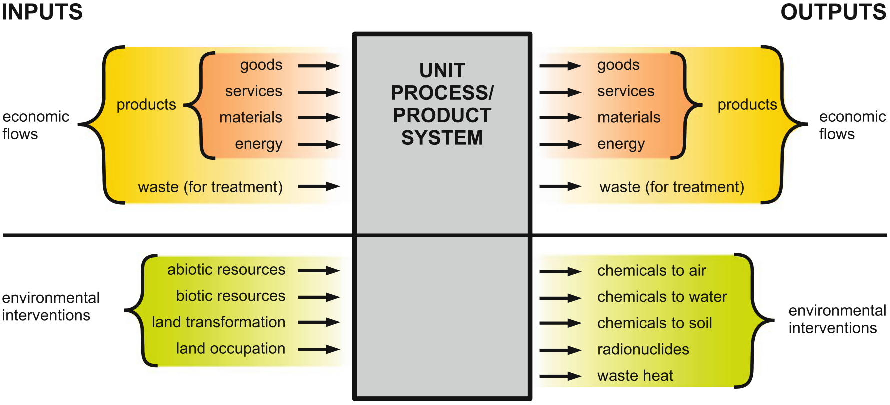

Fig. 1.3 Schematic illustration of a unit process in life-cycle assessment showing economic and environmental inflows balanced with the corresponding economic and environmental outflows (Adapted from Guinée and Heijungs 2005)

is affected directly by decisions based on or inspired by the study". The background system then consists of all other processes which interact with the foreground system "by supplying or receiving material and energy through a market" (Höjer et al. 2008).

The life-cycle assessment approach itself can be subdivided into two types: attributional and consequential LCA (Finnveden et al. 2009). An attributional LCA has a descriptive focus, depicting the environmental impact of all flows that are attributed to a certain amount of functional unit. A consequential LCA is change-oriented and estimates the system-wide change in environmental impact resulting from a modification of the amount of functional unit produced in response to possible different decisions. In attributional LCA, scaling the results linearly is possible, while consequential LCA focuses on marginal changes and the results therefore depend on the magnitude of change (Rebitzer et al. 2004).

The methodology has been standardised by the International Standards Association (ISO 14040) into a framework of four interdependent phases (Guinée et al. 2002; Reap et al. 2008). Firstly in the g*oal and scope* phase the ambit of the analysis, as well as establishing in what way it will be applied, is designated. The system boundaries, function, functional unit and reference flow of the product system under study are set. The system boundary marks the limit defined between the environment and the physical economy within which the product system lies. All flows have their origin and end in the environment. The flows bridging this boundary will be environmental interventions, namely extraction of resources, emissions to the environment and the use of land (Guinée and Heijungs 2005). In general, when human intervention takes place this can be regarded as an economic process and not part of the natural environment. Thus controlled landfills, wastewater treatment, agriculture and forestry and mining tips are typically not included in the natural environment (Guinée et al. 2002). The functional unit is based on the function provided by the product or service, and need not be a mass-based quantity of material (Guinée and Heijungs 2005). The functional unit indicates the quantity of the function under consideration in the life-cycle assessment. The functional unit allows different systems to be considered functionally equivalent and allows reference flows to be set for each of them, thus enabling comparison of their environmental performance.

In the second phase of *life-cycle-inventory analysis* the flow of material and energy into, through, and from a product system is collated and quantified conforming to the definition of the goal and scope. This requires the determination of the system boundary, the representation of the system of unit processes with a flowchart, data gathering of unit process data and the performance of necessary allocations for any multifunctional unit processes.

In the third phase, *life-cycle-impact assessment,* the inventory data is converted into potential environmental impact estimates by means of a two-step process of classification and characterisation using cause-effect models. The outcomes can be further normalised, grouped and weighted into aggregated indicators reflecting consensual value preferences.

In the final phase of *life-cycle-interpretation* the results are evaluated for consistency and completeness and analysed for robustness. Conclusions are drawn and recommendations based upon the inventory and impact assessment data can be made. Typically iteration between life-cycle interpretation and the other life-cycle-assessment phases is often carried out.

1.3.2 Life-Cycle Assessment Applied to Emerging Technologies

Applying life-cycle assessment effectively ex post has its own implicit demands and these are magnified in ex ante applications when more uncertainties are involved. The potential of applying life-cycle assessment ex ante is recognised but also its limitations. The standard problems of ex post life-cycle assessment involving system boundaries, scaling issues, data availability and uncertainty are magnified when applied ex ante owing to unknown future technologies at the industrial scale and larger data gaps that further increase uncertainty (Hetherington et al. 2013). Problems can emerge from three areas: difficulties in defining the goal and scope of the life-cycle assessment at such an early developmental stage; uncertainty involving the data which may be of poor quality, resulting in dubious potential environmental impacts; and the establishment of an accurate level of confidence in data interpretation (Cinelli et al. 2014). There is a mismatch between the capability of the tools for analysis available and the fact that typically 80% of the environmental impacts are determined at the early development stage (Tischner et al. 2000). Differences between laboratory systems and industrial processes are crucial to data validity. At the lab scale, yields are typically lower than at industrial level, where efficiency gains have been integrated (Frischknecht et al. 2009). Scaling up can uncover by-products which require addressing by allocation. Also small variations in lab measurements or from model simulations may be amplified to large data errors. The impacts of specialised equipment and instrumentation may also be underestimated. Lab experiments are typically done in batches and are less efficient than typical continuous industrial-scale processes. Methods for tackling scaling issues have been proposed in studies of scaling behaviour of furnaces and heat pumps (Caduff et al. 2014) or a more general prognostication approach and a method with guidelines for going from pilot plants to industrial scale (Shibasaki et al. 2007).

Hospido et al. (2009) have recommended an approach with the following five guidelines for ex ante life-cycle assessment. The life-cycle assessment should be forward looking and descriptive, termed “prospective attributional LCA”. The functional unit should be a physical quantity or have an economic dimension. Scenarios should be applied to define a relevant future state. System boundaries can exclude unit processes that are not affected by the novel process. The foreground system should be modelled with specific data, while the background system should use average data.

The combinatorial and aggregative nature of the analysis brings with it data uncertainty at the laboratory level, after scaling up, and of the life-cycle assessment modelling itself, that seriously brings into question the validity of the results. Such limitations should be recognised and made explicit to all stakeholders involved (Hetherington et al. 2013). This does not necessarily negate the value of exploratory studies which can be later added to and corrected cumulatively by further research.

A second-order analysis can involve uncertainty analysis and validity of data at all levels to determine the general confidence in the final outcomes of the proposed research. At the life-cycle assessment level, statistical estimates of uncertainty can also be applied as outlined in the following section.

1.3.3 Uncertainty Issues in Life-Cycle Assessment

The practice of life-cycle assessment deals with and delivers its quantified information as point values, rarely reflecting variability or a spread of possible values (Henriksson et al. 2013). Recognition of the existence of such variabilities means acknowledging uncertainty. Uncertainty can be subdivided into two types which are not mutually exclusive. Epistemic uncertainty relates to the incompleteness of knowledge, while stochastic uncertainty pertains to the inherent randomness of the natural world. Stochastic uncertainty can relate to spatial or temporal variability (Clavreul et al. 2012). Epistemic uncertainty loops back to uncertainty itself, as the estimation of uncertainty is in itself a source of uncertainty (Björklund 2002).

The results of a life-cycle assessment can be uncertain owing to data variability, error in measurements, incorrect estimations, modelling assumptions, outdated data, unrepresentative data and data gaps (Finnveden et al. 2009). The cumulative nature of the methodology means that uncertainty can build up and combine to become manifest at all levels of life-cycle assessment. For example the data inputs can be inaccurate, missing, outdated or unrepresentative. Averaging is often done without acknowledging the spatial and temporal heterogeneity of the data source. Since life-cycle assessment is a tool founded on quantification, uncertainty is present at the data inventory level of the unit processes and also in the characterisation models, weighting factors and resulting potential impacts. The generation and use of more precise data is one way to tackle this type of uncertainty (Wender et al. 2014).

The simplifications implicit in life-cycle assessment are also a source of uncertainties. Its broad, non dynamic life-cycle perspective does not account for localised or temporal effects. For instance these are not aligned with the temporal frames of characterisation models with different time horizons (Guo and Murphy 2012). Its modelling assumes simple linear scaling of economic and environmental processes and its result should always be termed "potential" impacts, not specified in space and time. Standardisation of the methodology has been a way of curtailing arbitrariness requiring transparency about the choices made relating to goal and scope, system boundaries, the functional unit and allocation methods (Guinée et al. 2002).

Given all the aforementioned, the aggregative nature of the tool means that uncertainty can accumulate and combine within the modelling perceivable at all levels of life-cycle assessment. A taxonomy proposed by Huijbregts (1998) linking all of the above back to life-cycle assessment defined three groups of uncertainties:

- parameter uncertainties referring to the uncertainty in values because of inherent variability, measurement imprecision or lack of data, for example;
- scenario uncertainties owing to the necessary choices made to build scenarios; and
- model uncertainties owing to the mathematical models underlying life-cycle assessment calculations.

Finnveden et al. (2009) reinterpret these more broadly, referring to the sources of a life-cycle assessment where uncertainty may arise, namely data, choices and relations. Efforts can be made to improve the quality of the data (better measurements and models) and the choices made (stakeholder discussions to reach consensus on uncertainty) but this is often impractical in a short time frame. Thus the trend is to incorporate uncertainty into life-cycle assessment using probability and statistical methods.

Ways that uncertainty has been acknowledged involve replication of life-cycle assessment using scenarios where assumptions are changed one at a time to compare different outcomes (Clavreul et al. 2012), exploring and reporting the sensitivity of the outcomes to changes, and applying and incorporating statistical uncertainty analysis (Henriksson et al. 2013). Statistical techniques have been incorporated to evaluate the quality of the data of the life-cycle inventory. The uncertainty of the inventory data is represented by six characteristics (reliability, completeness, temporal, geographical and technological correlation and sample size). Each characteristic is divided into five levels with a score from 1 to 5. An uncertainty factor in terms of contribution to the square of the geometric standard deviation is given to each score of the six characteristics. By representing the data-quality-indicator value by a ‘default’ log normal distribution, this approach translates the data-quality indicators into probability distributions (Guo and Murphy 2012). Then the method stochastically propagates the probability distributions using random sampling such as Monte Carlo analysis (Clavreul et al. 2012).

Ultimately it is important to recognise that the outcome of a life-cycle assessment is not an absolute result. The value of the tool lies in its application to comprehensively compare systems, and its outcomes are useful in a relative sense in spite of the uncertainties. Moreover, it may also be argued that the shortcomings and incompleteness of life-cycle assessment instil a rigorous approach, compelling the practitioner to maintain focus and remain alert.

1.4 Illustrative Case Study Summary: Copper Recovery from Electronic Waste Using Bioleaching

Few life-cycle assessments have been carried out on metal-recovery techniques applied to electronic waste as summarised by Table 1.3.

The life-cycle assessment of metal recovery from printed circuit boards using pyrometallurgical techniques by Bigum et al. (2012) has shown that it has an improved environmental performance and also a greater yield than virgin mining. Such recycling and recovery is advised in view of resource criticality and a transition to a circular economy. If a biotechnological route can be shown to be competitive and environmentally benign relative to the existing pyrometallurgical method and other traditional techniques, this technology can be regarded as an improvement of methods of metal recovery applied to electronic waste treatment.

Bioprocesses for the recovery of metals from electronic waste are described elsewhere in this book. An illustrative case study by the author applied life-cycle assessment to a novel laboratory bioleaching process for metal recovery from printed circuit boards to determine its potential environmental performance (Villares et al. 2016). Using the laboratory process as a foundation, the potential environmental impacts of a plausible industrial scale version of the process were estimated for comparison with an established pyrometallurgical technology. To stimulate new paths of enquiry and to guide further development of the technology,

Table 1.3 Overview of life-cycle assessments carried out on metal recovery from electronic waste

Metal recovery technique	Remarks	References
Pyrometallurgical	Life-cycle assessment of the recovery of aluminium, copper, gold, iron, nickel, palladium and silver from high-grade electronic waste modelled on the Boliden smelter refinery at Rönnskär, Sweden.	Bigum et al. (2012)
Pyrometallurgical	Life-cycle assessment to quantify the environmental impacts of recovery of 17 metal products of the Umicore integrated precious metals smelter-refinery in Hoboken, Belgium using detailed industry data.	Stamp et al. (2013)
Hydrometallurgical	Life-cycle assessment of sulphuric acid leaching and selective precipitation for yttrium, zinc, copper, lithium, and cobalt from fluorescent lamps, cathode ray tubes, Li-ion accumulators and printed circuit boards.	Rocchetti et al. (2013)
Hydrometallurgical	Using literature data, a comparison of environmental performance of two processes for recovering copper from printed circuit boards, one using sulphuric acid and one using a mix of nitric and hydrochloric acid.	Rubin et al. (2014)
Hydrometallurgical	Life-cycle assessment of printed-circuit-board recycling chain in China for recovery of lead, zinc, copper, gold, palladium and silver using mechanical beneficiation, acid leaching and electrolysis.	Xue et al. (2015)

the scaled up novel bioleaching process was embedded in a larger product system of upstream and downstream processes and life-cycle assessment was applied.

Potential environmental hotspots were identified in the energy and material inputs for the bioleaching unit process, particularly the air input, and solvents for copper recovery. A pre-treatment stage of shredding of printed circuit boards contributed relatively marginally to potential environmental impacts. Bioleaching itself contributed to more than 50% of potential environmental impacts of eutrophication and acidification potential, photochemical oxidation, climate change and three toxicity categories: human, terrestrial and aquatic freshwater toxicity. Solvent extraction and electrowinning for recovery of elemental copper contributed around 80% to the potential depletion of abiotic resources and stratospheric ozone. The comparison with the existing pyrometallurgical technology returned an inferior environmental performance even after simulating a further optimisation by increasing the amount of printed circuit boards treated, all else remaining the same.

The estimations and uncertainties around the environmental performance of the scaled up bioleaching product system of the case study mean that it cannot be considered a definitive result. Nonetheless, Villares et al. (2016) propose that the insights gained can guide the further development of the bioleaching technique and contribute to developing secondary metal recovery from electronic waste in an environmentally responsible manner. Indeed, such broadening of the research domain of the novel bioleaching process the by study spurred thinking regarding its possible future optimisation. This includes further exploration of bioleaching mechanisms, adaptation of the microorganisms and exploring more effective naturally occurring bacterial consortia, improving the efficiency of the bioreactors, recovering and recycling process water and using waste products, such as biogenic sulphur as nutrient inputs.

1.5 Conclusion

The need for addressing the growing waste stream of electronic waste to effectively recover secondary materials taking advantage of the benefits of circularity and recycling have been discussed in this chapter. Life-cycle assessment can assist in evaluating future metal recovery alternatives but its application requires a well bounded and defined product or service system. At an early development stage, life-cycle assessment of not yet existent technologies that are sketchily defined do not provide the same type of results. However, the fact that it does provide useful insights when confronting such uncertainties obliges the early application of life-cycle assessment to be regarded as an instrument aiding in the making of a plausible mock up of the potential future technology and its possible future context. The case study serves to illustrate the benefits of applying life-cycle assessment to evaluate an emerging technology to guide its further development accounting for possible environmental impacts. The procedure should be reiterated shifting from the estimates of the early stage to newly acquired real data from the further development of the novel process. These later iterations of life-cycle assessment, refining previous work in later stages of technological development, should result in more confidence in the environmental performance results.

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Case Study Supplementary Information For extended information on the case study see master thesis with appendices available for download: http://repository.tudelft.nl/view/ir/uuid:ad116c32-ea7c-40eb-955a-ba96d62ac5c8/

References

Baldé CP, Wang F, Kuehr R, Huisman J (2015) The global e-waste monitor – 2014. United Nations. University, IAS – SCYCLE, Bonn

Bigum M, Brogaard L, Christensen TH (2012) Metal recovery from high-grade WEEE: a life cycle assessment. J Hazard Mater 207-208:8–14. doi:10.1016/j.jhazmat.2011.10.001

Binnemans K, Jones PT, Blanpain B, Van Gerven T, Yang Y, Walton A, Buchert M (2013) Recycling of rare earths: a critical review. J Clean Prod 51:1–22. doi:10.1016/j.jclepro.2012.12.037

Björklund AE (2002) Survey of approaches to improve reliability in LCA. Int J Life Cycle Assess 7:64–72. doi:10.1007/BF02978849

Bradshaw AM, Reuter B, Hamacher T (2013) The potential scarcity of rare elements for the Energiewende. Green 3:93–111. doi:10.1515/green-2013-0014

Breivik K, Armitage JM, Wania F, Jones KC (2014) Tracking the global generation and exports of e-waste. Do existing estimates add up? Environ Sci Technol 48:8735–8743. doi:10.1021/es5021313

Caduff M, Huijbregts MAJ, Koehler A, Althaus H-J, Hellweg S (2014) Scaling relationships in life cycle assessment. J Ind Ecol 18:393–406. doi:10.1111/jiec.12122

Castro-Molinare J, Korre A, Durucan S (2014) Sustainability analysis of copper extraction and processing using life cycle analysis methods: a case study in the North of Chile. In: 24th European symposium on computer aided process engineering – escape 24 June 15–18, 2014. Elsevier, Budapest, pp 1861–1866

Charles JA, Gill CB, Lorig CH, Shewmon PG (2014) Metallurgy. Enc Britannica:1–41

Cinelli M, Coles SR, Kirwan K (2014) Analysis of the potentials of multi criteria decision analysis methods to conduct sustainability assessment. Ecol Indic 46:138–148. doi:10.1016/j.ecolind.2014.06.011

Clavreul J, Guyonnet D, Christensen TH (2012) Quantifying uncertainty in LCA-modelling of waste management systems. Waste Manag 32:2482–2495. doi:10.1016/j.wasman.2012.07.008

Cui J, Zhang L (2008) Metallurgical recovery of metals from electronic waste: a review. J Hazard Mater 158:228–256. doi:10.1016/j.jhazmat.2008.02.001

Ellen MacArthur Foundation (2013) Towards the circular economy. economic and business rationale for an accelerated transition. Cowes, London

Erüst C, Akcil A, Gahan CS, Tuncuk A, Deveci H (2013) Biohydrometallurgy of secondary metal resources: a potential alternative approach for metal recovery. J Chem Technol Biotechnol 88:2115–2132. doi:10.1002/jctb.4164

European Commission (2014a) Report on critical raw materials for the EU. Report of the Ad hoc working group on defining critical raw materials. Brussels, Belgium

European Commission (2014b) Towards a circular economy: a zero waste programme for europe. communication from the commission to the european parliament, the council, the european economic and social committee and the committee of the regions, Brussels 2014. Brussels, Belgium

European Commission (2014c) Report on critical raw materials for the EU. Critical raw materials profiles. Brussels, Belgium

Finnveden G, Hauschild MZ, Ekvall T, Guinée J, Heijungs R, Hellweg S, Koehler A, Pennington D, Suh S (2009) Recent developments in life cycle assessment. J Environ Manag 91:1–21. doi:10.1016/j.jenvman.2009.06.018

Frischknecht R, Büsser S, Krewitt W (2009) Environmental assessment of future technologies: how to trim LCA to fit this goal? Int J Life Cycle Assess 14:584–588. doi:10.1007/s11367-009-0120-6

Ghosh B, Ghosh MK, Parhi P, Mukherjee PS, Mishra BK (2015) Waste printed circuit boards recycling: an extensive assessment of current status. J Clean Prod:1–15. doi:10.1016/j.jclepro.2015.02.024

Graedel TE, Harper EM, Nassar NT, Reck BK (2015) On the materials basis of modern society. Proc Natl Acad Sci U S A 112:6295–6300. doi:10.1073/pnas.1312752110

Guinée J, Heijungs R (2005) Life Cycle Assessment (LCA). In: Kirk-Othmer Encyclopedia of Chemical Technology, Concise 5th Edition Wiley-VCH, pp 805–831

Guinée JB, Gorrée M, Heijungs R, Huppes G, Kleijn R, de Koning A, van Oers L, Wegener Sleeswijk A, Suh S, Udo de Haes HA, de Bruijn H, van Duin R, Huijbregts MAJ, Lindeijer E, Roorda AAH, van der Ven B, Weidema BP (2002) Handbook on Life Cycle Assessment. Operational Guide to the ISO Standards. Dordrecht, Kluwer Academic Publishers

Guinée JB, Heijungs R, Huppes G, Zamagni A, Masoni P (2011) Life cycle assessment: past, present, and future. Environ Sci Technol 45:90–96. DOI: 10.1021/es101316v

Guo M, Murphy RJ (2012) LCA data quality: sensitivity and uncertainty analysis. Sci Total Environ 435-436:230–243. doi:10.1016/j.scitotenv.2012.07.006

Hadi P, Xu M, Lin CSK, Hui C-W, McKay G (2015) Waste printed circuit board recycling techniques and product utilization. J Hazard Mater 283:234–243. doi:10.1016/j.jhazmat.2014.09.032

Hall WJ, Williams PT (2007) Separation and recovery of materials from scrap printed circuit boards. Resour Conserv Recycl 51:691–709. doi:10.1016/j.resconrec.2006.11.010

Henriksson PJG, Guinée JB, Heijungs R, de Koning A, Green DM (2013) A protocol for horizontal averaging of unit process data-including estimates for uncertainty. Int J Life Cycle Assess 19:429–436. doi:10.1007/s11367-013-0647-4

Hetherington AC, Borrion AL, Griffiths OG, McManus MC (2013) Use of LCA as a development tool within early research: challenges and issues across different sectors. Int J Life Cycle Assess 19:130–143. doi:10.1007/s11367-013-0627-8

Höjer M, Ahlroth S, Dreborg K-H, Ekvall T, Finnveden G, Hjelm O, Hochschorner E, Nilsson M, Palm V (2008) Scenarios in selected tools for environmental systems analysis. J Clean Prod 16:1958–1970. doi:10.1016/j.jclepro.2008.01.008

Hospido A, Davis J, Berlin J, Sonesson U (2009) A review of methodological issues affecting LCA of novel food products. Int J Life Cycle Assess 15:44–52. doi:10.1007/s11367-009-0130-4

Huijbregts MAJ (1998) Analysis of uncertainty and variability in life cycle assessment. Int J Life Cycle Assess 3:273–280, https://doi.org/10.1007/BF02979835

Ilyas S, Lee J (2014a) Biometallurgical recovery of metals from waste electrical and electronic equipment: a review. ChemBioEng Reviews 1:148–169. doi:10.1002/cben.201400001

Ilyas S, Lee J (2014b) Bioleaching of metals from electronic scrap in a stirred tank reactor. Hydrometall 149:50–62. doi:10.1016/j.hydromet.2014.07.004

Işıldar A, van de Vossenberg J, Rene ER et al (2015) Two-step bioleaching of copper and gold from discarded printed circuit boards (PCB). Waste Manag. doi:10.1016/j.str.2014.12.012

International Organisation for Standardization (ISO) (2006) ISO 14040 Environmental management – life cycle assessment – principles and framework. Geneva, Switzerland

Kiddee P, Naidu R, Wong MH (2013) Electronic waste management approaches: an overview. Waste Manag 33:1237–1250. doi:10.1016/j.wasman.2013.01.006

Kleijn R (2011) Metal requirements of low-carbon power generation. Energy 36:5640–5648. doi:10.1016/j.energy.2011.07.003

Kleijn R, Van der Voet E (2010) Resource constraints in a hydrogen economy based on renewable energy sources : an exploration. Renew Sust Energ Rev 14:2784–2795. doi:10.1016/j.rser.2010.07.066

Lee J-C, Pandey BD (2012) Bio-processing of solid wastes and secondary resources for metal extraction – a review. Waste Manage (New York, NY) 32:3–18. doi: 10.1016/j.wasman.2011.08.010

Li J, Zeng X (2012) Recycling printed circuit boards. In: Waste Electrical and Electronic Equipment (WEEE) Handbook. Woodhead Publishing Ltd, Cambridge, pp 287–311

Mishra D, Rhee YH (2014) Microbial leaching of metals from solid industrial wastes. J of Microbiol 52:1–7. doi:10.1007/s12275-014-3532-3

Moss RL, Tzimas E, Willis P, Arendorf J, Tercero Espinoza L (2013) Critical metals in the path towards the decarbonisation of the EU energy sector, JRC Scientific & Policy Report. European Commission, Luxembourg

Ongondo FO, Williams ID, Cherrett TJ (2011) How are WEEE doing? A global review of the management of electrical and electronic wastes. Waste Manag 31:714–730. doi:10.1016/j.wasman.2010.10.023

Petersen J (2010) Modelling of bioleach processes: Connection between science and engineering. Hydrometall 104:404–409. doi:10.1016/j.hydromet.2010.02.023

Ravi V (2012) Evaluating overall quality of recycling of e-waste from end-of-life computers. J Clean Prod 20:145–151. doi:10.1016/j.jclepro.2011.08.003

Reap J, Roman F, Duncan S, Bras B (2008) A survey of unresolved problems in life cycle assessment. Part 1: Goal and scope and inventory analysis. Int J Life Cycle Assess 13:290–300. doi:10.1007/s11367-008-0008-x

Rebitzer G, Ekvall T, Frischknecht R, Hunkeler D, Norris G, Rydberg T, Schmidt W-P, Suh S, Weidema BP, Pennington DW (2004) Life cycle assessment part 1: framework, goal and scope definition, inventory analysis, and applications. Environ Int 30:701–720. doi:10.1016/j.envint.2003.11.005

Reck BK, Graedel TE (2012) Challenges in metal recycling. Science 337:690–695. doi:10.1126/science.1217501

Reuter M (2013) Metal recycling: Opportunities, limits, infrastructure. report 2b of the global metal flows working group of the international resource panel of UNEP. Paris, France.

Robinson BH (2009) E-waste: an assessment of global production and environmental impacts. Sci Total Environ 408:183–191. doi:10.1016/j.scitotenv.2009.09.044

Rocchetti L, Vegliò F, Kopacek B, Beolchini F (2013) Environmental impact assessment of hydrometallurgical processes for metal recovery from WEEE residues using a portable prototype plant. Environ Sci Technol 47:1581–1588. doi:10.1021/es302192t

Rubin RS, De CMAS, Brandão D, Schalch V, Ometto AR (2014) Utilization of life cycle assessment methodology to compare two strategies for recovery of copper from printed circuit board scrap. J Clean Prod 64:297–305. doi:10.1016/j.jclepro.2013.07.051

Shibasaki M, Fischer M, Barthel L (2007) Effects on life cycle assessment - scale up of processes. In: Advances in Life Cycle Engineering for Sustainable Manufacturing Businesses. Proceedings of the 14th CIRP Conference on Life Cycle Engineering, Waseda University, Tokyo, Japan, June 11th–13th, 2007, 1st edn. Springer, London, pp 377–381

Stamp A, Althaus HJ, Wäger PA (2013) Limitations of applying life cycle assessment to complex co-product systems: The case of an integrated precious metals smelter-refinery. Resour Conserv Recycl 80:85–96. doi:10.1016/j.resconrec.2013.09.003

Stewart R (2012) EU legislation relating to electronic waste: the WEEE and RoHS Directives and the REACH regulations. In: Waste Electrical and Electronic Equipment (WEEE) Handbook. Woodhead Publishing Ltd, pp 17–52

Tischner U, Masselter S, Hirschl B (2000) How to do EcoDesign? A guide for environmentally and economically sound design. Verlag form: Frankfurt am Main, Germany

Tuncuk A, Stazi V, Akcil A, Yazici EY, Deveci H (2012) Aqueous metal recovery techniques from e-scrap: Hydrometallurgy in recycling. Miner Eng 25:28–37. doi:10.1016/j.mineng.2011.09.019

Udo de Haes HA, Heijungs R (2009) Analysis of physical interactions between the economy and the environment. In: Boersema JJ, Reijnders L (eds) Principles of Environmental Sciences Springer Science + Business Media BV, pp 207–237

Van der Voet E (2013) Environmental risks and challenges of anthropogenic Metals flows and cycles. report 3 of the global Metal flows working group of the international resource panel of UNEP. Paris, France

Van Leeuwen CJ (2007) Chapter 1: General introduction. In: Van Leeuwen CJ, Vermeire TG (eds) Risk assessment of chemicals: An introduction, 2nd edn. Springer, Berlin/Heidelberg/New York, pp 1–36

Villares M, Işıldar A, Mendoza Beltran A, Guinee J (2016) Applying an ex-ante life cycle perspective to metal recovery from e-waste using bioleaching. J Clean Prod 129:315–328. doi:10.1016/j.jclepro.2016.04.066

Watling HR (2006) The bioleaching of sulphide minerals with emphasis on copper sulphides - A review. Hydrometall 84:81–108. doi:10.1016/j.hydromet.2006.05.001

Wender B, Foley RW, Prado-López V, Ravikumar D, Eisenberg DA, Hottle TA, Sadowski J, Flanagan WP, Fisher A, Laurin L, Bates ME, Linkov I, Seager TP, Fraser MP, Guston DH (2014) Illustrating anticipatory life cycle assessment for emerging photovoltaic technologies. Environ Sci Technol 48:10531–10538. DOI: 10.1021/es5016923

Widmer R, Oswald-Krapf H, Sinha-Khetriwal D, Schnellmann M, Böni H (2005) Global perspectives on e-waste. Environ Impact Assess Rev 25:436–458. doi:10.1016/j.eiar.2005.04.001

Xue M, Kendall A, Xu Z, Schoenung JM (2015) Waste management of printed wiring boards: A life cycle assessment of the metals recycling chain from liberation through refining. Environ Sci Technol 49:940–947. doi:10.1021/es504750q

Zeng X, Zheng L, Xie H, Lu B, Xia K, Chao K, Li W, Yang J, Lin S, Li J (2012) Current status and future perspective of waste printed circuit boards recycling. Procedia Environ Sci 16:590–597. doi:10.1016/j.proenv.2012.10.081

Chapter 2
Adsorption Technology for Removal of Toxic Pollutants

Ansar Anjum

Abstract Metals present in natural waters are nondegradable, unlike organic compounds. These metals lead to somatic cell mutation that causes increased cancers amongst children throughout the world. The existing remediation methodologies for removal of such toxic metals are oxidation, coagulation and flocculation, precipitation, ion exchange, membrane filtration, ozone oxidation and bioremediation. Most of the methods involve production of high metal-contaminated sludge and high maintenance cost or the use of a relatively expensive mineral matrix that offset the performance and efficiency advantages. Adsorption has largely emerged as significant technology for removal of toxic metals. The review of over 240 published studies (1982–2016) shows an exhaustive list of adsorbents in the literature, including chitosan, fly ash, used tyre rubber, wood char, rice husk, aluminosilicates, etc. This review shows that the modification of most of the adsorbents offers outstanding performances to solve heavy metal related pollution issues. The removal of toxic metals using natural adsorbents is economical and environment friendly. Treated clay shows increased removal of metal ions under the same conditions compared to the untreated clay minerals due to increased surface area. One of the best adsorption capacities reported for As is 95% from 1 mg/L using hybrid adsorbents, 98% of Sb from 0.05 mg/L using hydroxyapatite and 97% of Cd from 10 mg/L using *A. rubescens* biomass.

Keywords Adsorption • Antimony • Arsenic • Cadmium • Efficiency • Lead • Modified adsorbents • Mercury • Phenolic compounds • Zinc

Contents

A. Anjum (✉)
Department of Applied Science and Humanities, Galgotias College of Engineering and Technology, Greater Noida 201306, India
e-mail: ansaranjum_a@rediffmail.com

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2.1 Introduction

The development of science and technology has led to intensified environmental pollution as well as deterioration of many ecosystems with accumulation of pollutants such as heavy metals and synthetic compounds. According to the United Nations World Water Development Report in 2003, almost two million tons of waste is disposed off within receiving waters per day including industrial, human and agricultural wastes. Many water bodies are contaminated with heavy metals that are toxic and carcinogenic such as arsenic, antimony, cadmium, chromium, lead, mercury, nickel and zinc. Thus, the removal of such metals from water has been documented as a priority issue by the World Health Organization that accounts to their urgent remediation.

Several remediation methodologies have been developed for removal of heavy metals from water; the most common are oxidation and sedimentation, coagulation and filtration, sorptive media filtration and membrane filtration. The detailed analysis of the mentioned methodologies does not potentially satisfy the essential critical requirements such as efficient removal of metal, low cost and easy maintenance, long life expectancy and high rate of metal removal, mechanical strength and large surface area. Moreover, they are incapable to disintegrate in water flow and overcome the changes in pH, hardness or microbiology that affect the water quality. However, most of the common methodologies adopted for the removal of heavy metals from water are expensive that increase the economic pressure on rural communities with high levels of toxicant in food and drinking water. Thus, amongst the approaches proposed, adsorption is one of the mostly adopted methods for remediation as it is found to be very effective, economical and versatile.

2.1.1 Background

The introduction of contaminants such as synthetic chemicals, non-biodegradable plastics and heavy metals into the natural environment that cause adverse changes is called pollution. Pollution can be toxic with varied toxicity defined as the degree to which a substance, i.e. a toxin or poison, can harm humans or animals. It is often described as *point source* (that enters the water body from a specific site) or *diffuse* or *non-point pollution* (arise where substances are widely used and dispersed over an area). Commonly encountered heavy metals are arsenic, antimony, chromium, cobalt, mercury, selenium, cadmium, zinc and lead. Valko et al. (2006) state that heavy metals are a heterogeneous group of highly reactive substances that may act as essential cofactor for physiologic processes and/or as toxic elements. Some metals exhibit toxicity by inducing oxidative stress directly such as iron redox cycling between Fe^{3+} and Fe^{2+} that create superoxide (O_2^-) in the process. Some metals undergo redox-cycling reactions under physiological conditions such as iron (Fe), copper (Cu), chromium (Cr), vanadium (V) and cobalt (Co). There are other metals such as mercury (Hg), cadmium (Cd), nickel (Ni) and arsenic (As) that increase oxidative stress indirectly by depleting glutathione and bonding to sulfhydryl groups of proteins. Such metals are considered as toxic pollutants as they are not essential for biological functions (Ahsan et al. 2006).

Heavy metals are introduced into the environment through products of mining, smelting and refining of fossil fuels, production and use of metallic commercial products and vehicular exhaust products, domestic sewage, industrial effluents and thermal power plants, agricultural and animal wastes, coal ashes and fertilizers. Arslanoglu et. al. (2009) described the heavy metal binding properties of esterified lemon Babel et al. (2003), Wan et al. (2008) and Bhattacharyya et al. (2008) show studies on the removal of heavy metals that have been investigated using chemical precipitation and physical treatment such as ion exchange, solvent extraction, osmosis and adsorption. The process of coagulation used for removal of heavy metal generates toxic sludge that adds supplemental toxic substances back to the environment. The treatment of water by membrane filtration involves synthetic membrane filters with appropriate pore size, and thus it becomes an expensive technique membrane.

2.1.2 Issues and Problems

A multitude of scientific publications and popular articles appeared during the last three decades on metal pollution and their respective toxicity. The increased concentrations of heavy metals in water have triggered a worldwide campaign for innovative water management practices.

In 2001, a TNN report says that out of 20,000 metal-contaminated sites in England, 38% of the sites have been found to be located in groundwater areas. Another recent survey in the United States reports 79% of 727 samples of surface water are contaminated with arsenic. The metal concentration may be present up to

500 mg/kg of soil, either as dissolved in the soil solution, exchangeable in structural components of the lattices of soil minerals or as insoluble precipitates with other soil components. Aydinalp and Marinova (2003) reported that the heavy metals that are in dissolved and exchangeable forms are available to plants, whereas the metals that compose the structural components of lattices of soil minerals or exist as insoluble precipitates with other soil components are potentially available in the longer term. This leads to contamination of groundwater supply of nearby human-inhabited areas in many countries where most of the water supplies originate from rivers and streams.

A research by Stollenwerk (1994) at mine sites reports 20,000–50,000 sites in the United States where heavy metals are introduced to groundwater. The plume of acidic water (pH = 2–3) contains very high concentrations of aluminium, cobalt, copper, iron, manganese, zinc and nickel (>2000 mg/L). The plume from copper mining migrates through the water bodies; the oxidation of reduced iron occurs by manganese oxides in the sediment. The acidic water reacts with carbonate minerals in soil, and sorption of hydrogen ions on precipitated iron increases the pH to 5–6. This affects the sorption reactions of aqueous copper, cobalt, nickel and zinc that depend on the increase in pH. Hence, aluminium precipitates out and is slowly introduced to the aquifer solids. Certain industrial processes release toxic heavy metals in the environment as listed in Table 2.1. A study at the Department of Environment (1995) reports that oil refineries are likely to be the largest source of vanadium to the environment.

The United States share the maximum percentage of refinery capacity per day, together with China as shown in Table 2.2. China has been the largest producer of lead (3000 metric tons) in 2013. According to a joint report published by the FAO, the United Nations Environment Programme (UNEP) and the World Health Organization (WHO) in 2013, the maximum consumption of insecticides (22,549 tons) is reported to be in Japan, whereas France shows the maximum consumption of herbicides (26,808 tons) in 2007. A study by the Blacksmith Institute Assessment

Table 2.1 Industrial activities that release heavy metals to the environment

Industry/process	Major countries affected	Contaminating metals/ metal compounds
Oil refineries spent catalyst	The United States, China, Russia, Japan, India, South Korea, Italy, Saudi Arabia, Germany, Canada	Vanadium
Lead works	China, Australia, the United States, Peru, Mexico, India, Bolivia, Russia, Sweden, Poland, South Africa, Ireland, Canada	Lead, arsenic, cadmium, sulphides, sulphates, chlorides
Pesticide manufacturing works	The United States, Africa, Brazil, France, Calamari, Naeve	Arsenic, copper, sulphate, thallium
Dye works, waste batteries, zinc smelting, e-waste	The United States, Mexico, China, India	Aluminium, cadmium, mercury

Source: Department of Environment (1995)

Process (2010) in low- and middle-income countries suggests that 56 million people in Europe are at risk of cadmium, arsenic, lead and mercury poisoning. The total emission of 575 tons of arsenic in the environment in Europe was reported in 1990. A study by Jarup (2003) shows that more than 100 million people have been affected by arsenic contamination in several member countries of the European Union in the 1980s.

Besides the industrial sources listed in Table 2.1, lead is also introduced through gasoline additives, can solder, ceramic glass, cosmetics and the battery/plastic recycling industry. According to a study by Krishnaswamy and Kumar (1998), many cosmetics like talcum powder, lipsticks, shampoos "kajal" and hair colour contain heavy metals. This has resulted in a growing number of cases of different kinds of cancer, tumours and some genetic disorders with high pace.

The ubiquitous presence of heavy metals in the environment and their widespread toxicity has led to numerous approaches for its remediation. Out of the removal methodologies, adsorption shows the possibility of regeneration and reuse of adsorbents along with low capital cost. Hence, adsorption has acquired global importance for minimization of the contamination of the environment. It has become a significant addition to green chemistry endeavours.

2.1.3 State of Metal Pollution

Metals are ubiquitous in the environment primarily trapped in some stable form in rocks, soils and sediments. The metals are introduced into the environment through geological and anthropogenic sources. Vahter (2008) reports that arsenic is released into the environment through volcanic activity, erosion of rocks and forest fires. Soil erosion and leaching contribute to 612×10^8 g/year and 2380×10^8 g/year of arsenic, respectively. A report by Khan (1996) states that elevated concentration, of arsenic in Bangladesh and West Bengal (India) in groundwater is the consequence of the ignorance of standard water testing procedures that did not include tests for any toxic metal. The geological and hydrological survey discovered a 450 km long layer of arsenic-rich silt clay, between 21 m and 61 m below the surface of the delta.

Table 2.2 Refinery capacity of the countries with oil refineries

Countries	Percentage of refinery capacity per day
United States	18.8
China	12.5
Russia	6.2
Japan	4.6
India	4.4
South Korea	3.1
Saudi Arabia	13
Canada	2.2

A study by Thornton (1992) shows that 9.5% of Japanese rice paddies have been rendered as incapable of producing consumable products.

Lead is largely introduced into water from atmospheric pollution, e.g. lead arsenate [$Pb_3(AsO_4)_2$], an insecticide. A research by Tong et al. (2000) indicates that 70% of lead in water and over 50% of many of the other trace metals in the Great Lakes are derived from atmospheric transfer. *Arsenic* ranks 20th in natural abundance comprising about 0.00005% of the Earth's crust as stated by Bromssen et al. (2007). It is introduced through various potential sources in waterways such as industrial mining and smelting operations including dissolution of pyrites, minerals and ores, effluents of coal, iron and other metal mining industries, burning of fossil fuels, heat-resistant alloys, antifouling paints, textile printing pigments, pulp and paper production, as depicted in Fig. 2.1.

Antimony is present in various oxidation states. A source study by Deorkar and Tavlarides (1997) states that the total consumption of antimony in various industrial products is 100,000 tons per year worldwide. Smichowski (2008) reports the elevated concentration of antimony in water as well as soils around mining and smelter areas at shooting ranges and along roadsides (dust from brake pads and tyres). Gebel (1997) describes the chemico-toxicological similarity of antimony with arsenic-clastogenic, but not mutagenic, carcinogenic potential. *Aluminium* pollution is associated with bauxite mining with steady increase in demand for aluminium in India. India ranks sixth in bauxite mining and eighth in aluminium production. Orissa in India is the worst aluminium affected state. The *cadmium* total input rate as reported by Hooda and Alloway (1998), Candinas et al. (1999), Eckel (2005), Lijzen and Ekelenkamp (1995) and Wilcke and Dohler (1995) in Germany is

Fig. 2.1 Champagne Pool Waiotapu near Rotorua (North Island of New Zealand). Silica sinter (*white*) with encrustations of arsenic-rich mineral material (*orange*) deposited from cooling water. Arsenic is a common pollutant in streams draining thermal areas (Source: http://en.wikipedia.org/wiki/Champagne_Pool)

500 g/km^2 followed by the Netherlands (450 g/km^2). According to Aylett (1979), cadmium was used in the 1940s in many industries, and it is only during the last three decades that serious consideration has been given to cadmium as an environmental contaminant. It is a recognized renal toxicant (WHO 1992). The maximum contaminant level (MCL) of cadmium assigned by the US Environmental Protection Agency (EPA) and Canada is 5 ppb, but this value was decreased to 3 ppb by the World Health Organization (WHO) in 1993. Chromium (pentavalent) is 100-fold more toxic than the trivalent form as reported by Petrilli and De Flora (1978). The chromium is introduced to the environment from textile industry (Barnhart, 1997). Mercury occurs in the Earths' crust at a concentration of 0.08 mg/kg (Mason and Morre 1982). It is used as slimicides and fungicides for many organisms. Atmospheric mercury is usually produced during mining and refining and incineration of garbage containing electrical equipment. Venezuelan crude oil has the highest vanadium content of 1400 mg/kg (Robert 2000). In Member States of the European Community, the different concentration ranges are remote areas 0.001–3 ng/m^3, urban areas 7–200 ng/m^3 and industrial areas 10–70 ng/m^3, respectively (Lahmann et al. 1986). Concentrations up to 2 μg/m^3 of vanadium have been reported in several cities in the Northeastern United States.

2.2 Existing Methodologies for the Removal of Toxic Metals

2.2.1 Oxidation

Most of the methodologies adopted for the removal of toxic metals perform better with anionic species than uncharged species at circum-neutral pH values. Therefore, a pre-oxidation step is required as the first treatment step before applying the main removal process to obtain toxic metal-free drinking water. Chlorine, ozone, potassium permanganate, manganese oxides and hydrogen peroxide have been used to accelerate oxidation of metals, including arsenic and antimony. A high oxidation efficiency is obtained using chlorine, but at the same time, the elevated concentrations of unwanted disinfection by-products with organic matter and the release of taste and odour compounds from algal cells should be considered. Potassium permanganate produces no harmful by-products but may give colour to water and cause filtration problems later in the treatment plant. Thus, oxidation alone cannot serve as a sufficient technology for the removal of metals though it may well be employed as a pretreatment step to increase the efficiency of the removal method. Copper, arsenic and lead may be removed separated by oxidation (Ahluwalia and Goyal 2007).

2.2.2 Coagulation-Filtration

Chemical precipitation through coagulation and filtration includes alum coagulation, iron coagulation and lime softening. Coagulants are substances capable of removing colloidal impurities from water, and coagulation is the process by which such removal is brought about. Co-precipitation occurs when an inorganic contaminant (e.g. arsenic) forms an insoluble complex (e.g. metal hydroxide flocs) with the coagulant. This may occur via adsorption inclusion or occlusion (Edwards 1994). Aluminium or ferric chlorides/sulphates can be added as coagulants, and following their addition, the relevant amorphous aluminium hydroxide [$Al(OH)_{3(am)}$] or ferric hydroxide [$Fe(OH)_{3(am)}$] is precipitated. Copper and zinc can be removed using coagulation (Adhoum et al. 2004).

The addition of aluminium or iron coagulants facilitates the conversion of soluble inorganic species of arsenic into insoluble products by precipitation, co-precipitation or adsorption. The formation of insoluble products facilitates the subsequent removal of metals from water by sedimentation and filtration processes. At high coagulant dosages, the adsorption of inorganic arsenic to precipitated metal hydroxide solids takes place, but entrapment of adsorbed contaminants in the interior of the growing particle and solid solution formation may also take place especially at low coagulant dosages.

Lime treatment is similar to coagulation with trivalent metal salts, but instead of metal hydroxides, hydrated lime ($Ca(OH)_2$) or $Mg(OH)_2$ is formed. The toxic metal removal mechanisms involve calcite precipitation (less effective) and sorption to $Mg(OH)_2$ solids (more effective). The process, however, does not serve as a major toxic metal removal mechanism due to low removal efficiencies and unfavourable operating conditions (very high pH and chemical dose rates are required).

Arsenate and antimonate removal is more effectively removed than As(III) and antimonite when using coagulation. Thus, a pre-oxidation step to oxidize As(III) to arsenate is beneficial as shown in Fig. 2.2.

The costs associated with this method include coagulation chemicals, pH adjustment before and after treatment, and sludge residue management. The methodology is advantageous as the monitoring of a breakthrough point is not required, whereas it requires low-cost chemicals.

The disadvantages of the methodology are that the procedure is effective only over a narrow pH range and coagulant dosage and the disposal of arsenic-contaminated coagulant (toxic) sludge poses problems. The presence of competing ions needs to be considered. As(III) needs to be oxidized to arsenate for effective removal. Hence, secondary treatment is necessary to meet the arsenic standard in lime treatment.

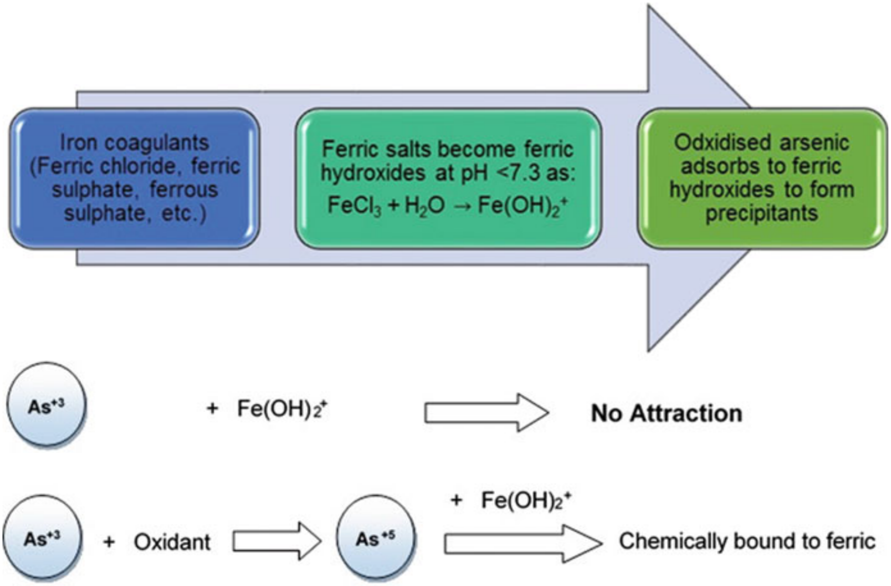

Fig. 2.2 Schematic of coagulation for removal of arsenic

2.2.3 Ion Exchange

Ion-exchange resins usually consist of a solid phase saturated with an anion that is exchangeable for metals in water as shown in Fig. 2.3. The media are regenerated with a solution of the exchangeable anion or replaced. An effective medium has a longer cycle between regenerations and thus capable of treating more bed volumes of water. It has high regeneration properties due to loss of media capacity. The resin has a preference for anions because of close charge spacing distance, functional group mobility and flexibility as well as the presence of hydrophilic groups (e.g. hydroxyl groups). Inglezakis and Grigoropoulou (2003) investigated the removal of lead from water by ion exchange.

The main disadvantage of ion exchange is that regeneration of resin and monitoring of breakthrough or filter use are required. It may be due to expensive technology depending on the resin/ion exchanger and is difficult to handle for some small systems. Oxidants may harm the ion exchanger if pre-oxidation is required. The removal of bicarbonate reduces the pH that increases the corrosiveness of treated wastewater. If the ion exchange is used beyond the point of sulphate exhaustion, the removed metal ion as arsenic may be released back into the treated water.

Fig. 2.3 Removal of As^{+3} from water using anion-exchange resin

2.2.4 *Membrane Processes*

Membrane processes include microfiltration, ultrafiltration, nanofiltration, reverse osmosis and electrodialysis. In these processes, the dissolved species are passed or retained by membranes based on the size, shape or charge of the compound.

Microfiltration and ultrafiltration exclude water constituents based on size which is 10–0.1 μm for microfiltration and 0.1–0.01 μm for ultrafiltration. Nanofiltration has a smaller pore size than microfiltration or ultrafiltration and can, therefore, exclude significant portions of dissolved metal as shown in Fig. 2.4. Potgieter et al. (2005) reported the removal of iron and manganese using nanofiltration membranes. However, it is more susceptible to fouling than microfiltration or ultrafiltration in reverse osmosis. The range of particles retained by reverse osmosis membranes lays between 0.005 and 0.5 μm including ions. In electrodialysis selective cation or anion membranes are used in integration with direct current electric field. Electrodialysis reversal simply means the polarity of the electric field is reversed to flush scale from the membrane. Electrodialysis and electrodialysis reversal have a similar particle size retention range to reverse osmosis.

The use of membrane processes for removal of metals may be desirable where microfiltration can be used to modify a process like coagulation, and multiple treatment objectives are necessary. Although the reverse osmosis unit is effective for a shorter time, it helps to improve the overall water quality by removing other constituents. It is disadvantageous due to the low ratio of treated product water to required inflow that is undesirable in areas with water shortages. The water pH does not affect removal in the range studied (4.0–8.0), although in the case of cellulose acetate membrane materials, it is pH selective (5.5–6.5) for arsenic. Advancements of membrane technology as electro-ultrafiltration possess good potential in removing arsenic from water (Weng et al. 2005).

The associated disadvantages of membrane processes are high operating and investment costs. The method usually requires a power source and controlled pressure, flow rate and pH. The guideline values are not met for high initial arsenic concentrations, whereas in water-scarce regions, the loss of influent water (20–25%) may be a concern. Pretreatment of the water may be necessary, e.g. for removing salts along with the readjustment of water quality after the treatment. Highly concentrated wastewater is produced at the reactor side and the membrane may not withstand the oxidant. Fouling must be considered for long-term use of membranes.

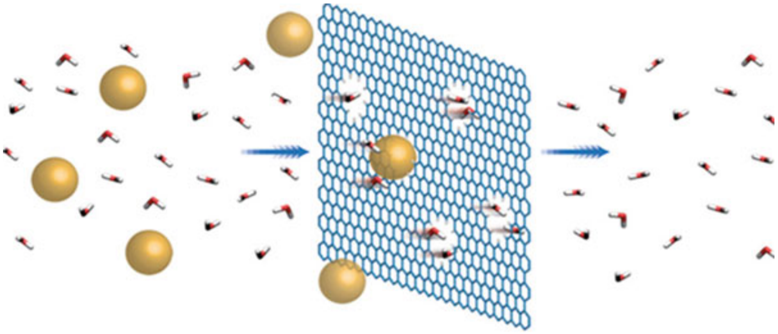

Fig. 2.4 Graphene membrane as a reverse osmosis membrane. Water molecules are driven to the *right* (*red* and *white*) and bigger molecules (*spheres*) are *left* behind (Wang and Karnik 2012)

2.2.5 Alternative Processes

Besides the methodologies discussed above, a few other alternative water treatment processes have been investigated for the removal of metals. Some alternatives involve variation of the implementation of existing treatments such as blending raw husk with contaminated water. This method is useful if a trace amount of pollutant like fluoride is desired in the effluent. Zero-valent iron is considered as a good adsorbent due to its high reactivity in water via spontaneous corrosion. When Fe(0) corrodes, FeOOH is produced on the surface, which has a good ability to adsorb metal(oid)s such as arsenic and antimony. Although Fe(0) is cheap and non-toxic, the necessary corrosion rate may be difficult to control for quantitative treatment of drinking water. Moving bed active filtration is a combination of co-precipitation and adsorption processes that utilize iron affinity for toxic metals like arsenic. The process includes a pre-reactor for introducing iron into the influent water and a moving bed sand filter. The sand filter is converted to an active filter by introduction of iron. Iron oxide-coated sand is continually formed abraded and regenerated within the filter.

Powdered alumina is also used followed by microfiltration wherein the influent water is mixed in a slurry with alumina particles below 200 μm diameter and then fed to a membrane unit for microfiltration. Alumina particles with bound metal ions are rejected by the filter and returned to the slurry reactor.

Another alternative process for the removal of toxic metals includes the biological treatment of water. Microbial mats immobilized on glass wool have been used to remove various metals and metalloids including arsenic from water. The studies suggest that arsenic may be removed from surface waters by phytoplankton with subsequent burial in lacustrine sediments. Phytoplankton either removes the metals by biological uptake and the organisms eventually settle or can act simply as particulate organic matter that adsorbs metals such as arsenic.

2.2.6 Adsorption

Adsorption is a mass transfer process in which a substance is transferred from a liquid phase to the surface of a solid and becomes bound by physical and/or chemical interactions. Adsorption is recognized as an effective and economic method for heavy metal waste water treatment. The process offers flexibility in design and operation and in many cases produces high-quality effluent. In addition, since adsorption is sometimes reversible, adsorbents can thus be regenerated by suitable desorption processes as mentioned by Fu and Wang (2011). Adsorption involves the passage of contaminated water through a bed of specially developed media where the contaminant (heavy metal) is adsorbed and removed from water. This generates two general types of residuals from media adsorption:

- Spent media
- Regeneration solutions

There are many performance measures of the ability of an adsorbent removal technology. The bed adsorption media is the number of bed volumes of water passed through a filter before the heavy metal concentration of effluent water is higher than a predetermined maximum contamination level. The metal removal capacity is a comparison of the amount of metal ion removed by weight or volume of media usually measured in “mg/litre” of wet media or “μg/grams” of dry media. The empty bed contact time is used to quantify the time required for the liquid in an adsorption bed to pass through the column assuming that there is proper dispersion and no preferential flow in the column. Adsorption has various advantageous features as:

- Low capital cost
- Ease of operation
- Effectivity and versatility
- Suitability for batch processes
- Generates less sludge
- Possibility of regeneration and reuse of adsorbent
- Potential to be applicable at very low concentrations

The adsorbent can be considered as cheap or low cost if it is abundant in nature and requires little processing or is a by-product of any industrial process. The reported literature of the last two decades has been compiled in this chapter that highlights the methodology of adsorption adopted for removal of heavy metal. A review of work re-counted for removal of heavy metals by adopting the methodology of adsorption has been premeditated with the details of research work performed by various authors using different adsorbents. The development of technologies for arsenic removal from industrial wastewater and contaminated drinking water has been the subject of several studies in the last decades.

2.3 Adsorbent Materials for Metal Removal

The adsorbents can be broadly classified as naturally occurring adsorbents; it includes the adsorbents that are obtained from natural resources as in Fig. 2.5. These can be used as treated or nontreated adsorbents, e.g. clay minerals and biosorbents. The chemically synthesized/modified adsorbents include chemical compounds or chemically synthesized adsorbents for adsorption, e.g. metal oxides and carbon nanotubes. Cationic hydrogels for arsenate removal from aqueous solution were studied by Barakat and Sahiner (2008).

Although the techniques mentioned earlier have been observed to be practical and cost-effective with concentrated wastewater, they are ineffective at low concentration wastewater that contains heavy metal ions less than 100 ppm. Many natural and/or synthetic adsorbents can effectively remove dissolved heavy metals, but most of them show some disadvantages such as poor adsorption capacity, low efficiency/cost ratio and ineffectiveness at high metal concentration. Thus selective adsorption utilizing various adsorbents including biological materials, mineral

Fig. 2.5 Adsorbents used for removal of metal from water: (**a**) activated alumina, (**b**) activated carbon, (**c**) rice hull, and (**d**) corncob

oxides, clay minerals, zeolite, fly ash, activated carbon or polymer resins has generated increasing interest.

The most common and effective method for removal of heavy metals from water is activated carbon, but it does not prove to be attractive due to high regeneration costs. This made biosorption to be investigated by researchers that use biomass as either living or dead microorganisms for removal of heavy metal ions from industrial wastewater. Several kinds of microorganisms (fungi, bacteria and algae) and bio-sludge of activated sludge systems have been reported to adsorb both organic and inorganic matter from wastewater. Dead biosorbents are more favourable as they are cheap, easily operated and not affected by the heavy metals. Moreover they can be regenerated and reused and are easily maintained.

Depending on the cell metabolism, the mechanisms of biosorption can be divided as metabolism dependent and non-metabolism dependent. On the basis of the ways for the metal to be captured by the cell, biosorption may be further classified according to the location of the metal ion removed from the solution as extracellular accumulation/precipitation or cell surface sorption/precipitation and intracellular accumulation.

Biochar by-products from fast wood/bark pyrolysis have been investigated as adsorbents for removal of As(III), Cd(II) and Pb(II) from water by Wang et al. (2015). Oak bark, pine bark, oak wood and pine wood char are obtained from fast pyrolysis at 400 °C and 450 °C in an auger-fed reactor. Maximum adsorption occurs over a pH range of 3–4 for arsenic and 4–5 for lead and cadmium. This study shows that the by-product char from bio-oil production can be used as plentiful inexpensive adsorbents for water treatment at a value above their pure fuel value. Igwe et al. (2005) reported the use of agricultural by-products for bioremediation of heavy metal ions that has proven to be an active field of interest. The methodology utilizes inactive (nonliving) microbial biomass that binds with heavy metals from waste streams by chelation and adsorption.

2.3.1 Adsorbents Used for Removal of Arsenic

Conventional and nonconventional treatment technologies for arsenic remediation have been compared in this section. The removal of arsenic from water involves specific adsorption by chemical attraction leading to bonds on specific sites of sorbents (Fig. 2.6).

Currently about 100 million people are consuming water with arsenic concentrations up to 100 times the concentration assigned by the guideline of the World Health Organization (10 μg/L) as cited by Kinniburgh and Smedley (2001). An article in Science by Ahmed et al. (2006) focuses on the problems of drinking water in Bangladesh. It demonstrates that two different approaches have had maximum impact, i.e. testing tube wells followed by switching away from contaminated wells to alternate uncontaminated water sources and the installation of deep wells that supply water from older aquifers that do not contain elevated arsenic levels.

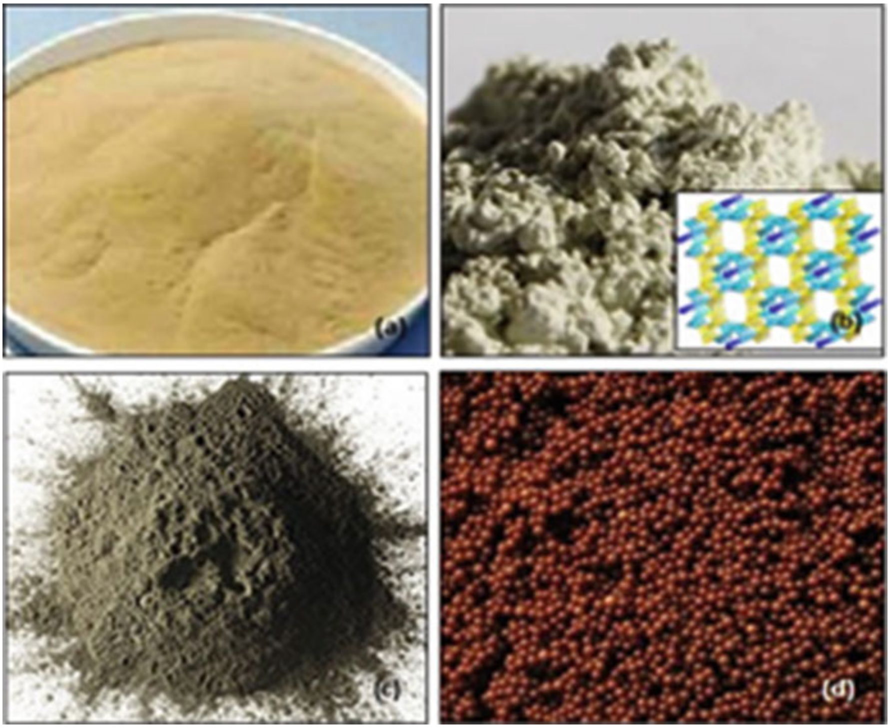

Fig. 2.6 (**a**) Palygorskite, (**b**) zeolite with structure as inset, (**c**) fly ash, and (**d**) polymer resin as adsorbents

Furthermore three major recommendations were made: (a) stimulate the periodic monitoring of water quality no matter what mitigation option exists, (b) encourage the wise use of deep aquifers low in arsenic, and (c) publicize widely the known effects of arsenic on the mental development of children. This illustrates that a variety of low-cost approaches must be employed in many developing locations throughout the world. When these approaches are exhausted, then adsorption is likely to contribute to further mitigation efforts.

Most of the technologies discussed in the literature are known to remove arsenic more effectively from water containing high initial arsenic concentrations (usually >100 mg/L), but residual arsenic concentrations exceed the 0.01 mg/L water quality standard used in most countries. Selective adsorption utilizing various adsorbents, including biological materials, mineral oxides, clay minerals, zeolites, fly ash, activated carbons or polymer resins has generated increasing interest (Fig. 2.6). It is observed that in villages of India and Bangladesh, a highly successful technology may not succeed in rural areas unless it fits into rural circumstances and is well accepted by the people. Technology development is only possible when a partnership exists involving proper village level participation. Hence, arsenic removal technologies all suffer from one or more drawbacks or limitations.

The effect of pH on the adsorption capacity depends on the surface charge or zeta potential of the sorbent at different pH and presence of different electrolytes. The number of available binding sites depends on the amount of sorbent taken. However, increasing the adsorbent dose can result in the formation of aggregates of the adsorbent. This leads to electrostatic interferences that diminish attractions between the adsorbing solute and the surface of the adsorbent. New resources such as hazelnut shell, rice husk, pecan shells, jackfruit, maize cob or husk have also been used as an adsorbent after chemical modification or conversion by heating into activated carbon for arsenic adsorption.

The theoretical calculations combined with instrumental analyses for removal of arsenic indicate inner-sphere complexation as a feasible mechanism for adsorption of arsenic on gibbsite as well as other adsorbents in the pH range from 5 to 9. The extended X-ray absorption fine structure EXAFS results indicate the formation of inner-sphere complexes of $As^{3+}$with gibbsite. Arsenic is coordinated to three oxygen atoms in the first shell at a distance of 1.77 Å and to aluminium in the second shell at a distance of approximately 3.20 Å in a bidentate-binuclear configuration for all evaluated pH values (5, 7 and 9). In addition, an $As\text{-}Al_2$ interaction is ascribed to a monodentate-binuclear complex due to its interatomic distance of 3.47 Å. This interaction of As^{3+} has also been observed with other adsorbents as well, such as montmorillonite and modified montmorillonite. The observed adsorption capacities for various sorbents are summarized in Tables 2.3 and 2.4, respectively.

The comparison of conventional and nonconventional treatment technologies for aqueous arsenic remediation by Ngo et al. (2002) shows that the first adsorbent that gained importance for successful removal of arsenic from water was granular-activated alumina. However, activated carbon has been used extensively for the removal of arsenic from water. Three types of activated carbons with different ash contents were studied by Lorenzen et al. (1995) for arsenic adsorption: coconut shell carbon with 3% ash, peat-based extruded carbon with 5% ash and a coal-based carbon with 5–6% ash. The removal of As(V) was observed to be higher using carbon with a high ash content, and its removal capacity increased after its pretreatment with Cu(II) as arsenic forms an insoluble metal arsenate with the impregnated copper. The optimum pH for arsenic adsorption by Cu-pretreated carbon was observed to be around 6.

Many adsorbents have been proposed and investigated during last two decades. Low-cost adsorbents that can be afforded in rural areas have been investigated as well. Agricultural products and their by-products have been used as low-cost adsorbents for the removal of arsenic from water. The adsorption efficiency using 0.1 g of rice husk was investigated by Nasir et al. (1997) from initial concentrations of 6.0×10^{-3} M arsenic. The adsorption follows the Freundlich isotherm over the concentration range from 8.7×10^{-5} M to 1.7×10^{-3} M arsenic ($K = 4.43$ mmol/g). An increase in temperature causes an increase in the removal of arsenic. Complete removal of arsenic [As(III) as well as As (V)] was achieved using 6 g

Table 2.3 Adsorptive removal of arsenic using naturally occurring adsorbents

Adsorbent used	Initial concentration	Efficiency of the adsorbent	Nature of investigation	References
Magnetic biochar	60 mg/L	0.27 mg/g	SEM-EDS TGA	Wang et al. (2015)
Modified peat	45 mg/L	90%	FT-IR	Ansone et al. (2013)
Zr-loaded orange waste gel	20 mg/L	4.2 mg/g	BET-SA ICP/AES	Biswas et al. (2008)
Maize cob wastes	500 μg/L	0.01 mg/g	AAS UV/VIS CHN	María and González (2008)
Maize leaves	50 mg/L	84.9%	FT-IR SEM	Kamsonlian et al. (2011)
Staphylococcus xylosus	100 mg/L	54.3 mg/g	FT-IR Titration	Aryal et al.(2010)
Rhodococcus sp.	100 mg/L	77.3 mg/g	FT-IR AAS	Prased et al. (2011)
Iron-impregnated potato peels	1 mg/g	0.11 mg/g	SEM WD/XRFS XRD	Dhoble et al. (2011)
Zeolite	150 mg/L	4.4 mg/g	AAS	Gülbas et al. (2011)
Aspergillus niger	0.10 mg/L	0.1 mg/g	AAS SEM TEM	Pokhrel and Viraraghavan (2008)
Human hair	0.360 mg/L	0.013 mg/g	TEM FT-IR HG/AF	Wasiuddin et al. (2002)
Chicken feathers	1.34 mM	27×10^5 M/g	XANES EXAFS	Teixeira and Ciminelli (2005)
Volcanic stone	0.2 mg/L	86%	ICP/AES	Elizalde-González et al. (2001)
Clinoptiloite-rich zeolitic tuff	0.360 mg/L	0.02 mg/g	XRD FT-IR UV/VIS	María and González (2008)
Kaolinite	2 mM	0.004 mol/Kg	ICP/AES HPLC	Kundu et al.(2004)
Sand	1.00 mg/L	17 mg/g	FT-IR SEM SEM	Gupta et al. (2012)
Iron oxide-coated sands	0.300 mg/L	0.009 mg/g	EDX ICP-OES	Hsu et al. (2008); Jessen et al. (2005)
Activated carbon	0.5 mg/L	0.03 mg/g	SEM BET	Ouma et al. (2011)
Mesoporous carbon	0.05 mg/L	8.1 mg/g	XRD HPLC HG/AFS	Gu et al. (2007)
Iron-modified activated carbon	22 mg/L	30 mg/g	AAS-HV ICP/MS	Chen et al. (2007)
Iron-impregnated mesoporous carbon	16 mg/L	8.0 mg/g	TEM FT-IR HG/AFS	Masih et al.(2009)
Powder activated carbon	5 g/L	8.4 mg/g	ICP-OES BET-N_2	Tien et al. (2004)
Limestone	520 mg/L	0.007 mg/g	AAS SEM	Hossain and Islam (2008)

(continued)

Table 2.3 (continued)

Adsorbent used	Initial concentration	Efficiency of the adsorbent	Nature of investigation	References
Biogenic manganese oxides	5 mg/L	0.1 mg/g	BET-SSA GF-AAS	Masue et al. (2007)
Oxides and clay minerals	0.020 mM	0.3 μmol/g	GF/AAS	Sabine Goldberg (2002)
Synthetic siderite	0.010 mg/mL	10.0 mg/g	SEM EDAX FT-IR	Guo et al. (2011)
Treated laterite	500 mg/L	8.4 mg/g	XRD SEM FT-IR TEM	Maiti et al. (2010)
Goethite	0.10 mM	0.0014 mmol/m^2	TGA DSC BET-N_2	Luxton et al. (2006)
Tropical soil	1 mg/L	97.6%	ICP-OES BET	
Natural laterite	0.20 mM	58%	ICP/MS GF/AAS	Goh and Lim (2004)
Red soil	100 mg/L	10%	TEM SEM BET -SSA	Singh et al. (2007)
Crushed crab shell chitosan	10 mg/L	6.2 mg/g	AAS	Rana et al. (2009)
Chitosan-coated ceramic alumina	1000 mg/L	56.5 mg/g	ICP/MS FT-IR XPS	Boddu et al. (2008)
Molybdate-impregnated chitosan beads	0.1 mg/L	95%	SSA ICP/AES	Jin Su et al. (2011)
Surfactant-modified MMT	100 mg/L	90%	XRD FT-IR SEM	Anjum et al. (2011)
MMT modified chitosan beads	10 mg/L	91%	XRD FT-IR-ATR SEM	Anjum et al. (2013)
Chitosan	400 mg/L	58 mg/g	XRD FT-IR	Chen and Chung (2006)
Tea fungal biomass	1.3 mg/L	1.1 mg/g	XRD SEM FT-IR TEM	Murugesan et al. (2006)
Shirasu zeolite	1.3 mM	66.0 mg/g	XRD SEM FT-IR TEM	Yan-hua Xu et al. (2002)
Penicillium purpurogenum	10–750 mg/L	35.6 mg/g	AAS SEM	Ridvan Say et al. (2003)
Olivier soil	5–100 mg/L	0.4 mg/g	EDX ICP-OES	Hua et al. (2006)
Sharkey soil	5–100 mg/L	0.74 mg/g	XRD ICP-OES	Hua et al. (2006)
Coconut coir pith anion exchanger	5–100 mg/L	13.6 mg/g	EDAX FT-IR	Anirudhan and Unnithan (2007)

(continued)

Table 2.3 (continued)

Adsorbent used	Initial concentration	Efficiency of the adsorbent	Nature of investigation	References
Pine wood char	10–100 mg/L	0.0012 mg/g	SEM FT-IR TEM	Mohan et al. (2007)
L. nigrescens	50–600 mg/L	45.2 mg/g	AAS SEM	Hansen et al. (2006)
Immobilized biomass	50–2500 mg/L	704.1 mg/g	AAS	Kamala et al. (2005)

Note: *AAS* atomic absorption spectroscopy; *FT-IR* Fourier Transform-InfraRed, *SEM* scanning electron microscopy, *EDAX* energy dispersive X-ray analysis, *XRD* X-ray diffraction, *ICP-OES* inductively coupled plasma-optical emission spectrometry, *TEM* transmission electron microscopy; *BET-SSA* Brunauer-Emmett-Teller-specific surface area, *GF/AAS* graphite furnace-atomic absorption spectroscopy, *HPLC* high-performance liquid chromatography, *DSC* differential scanning calorimetry, *XRFS* X-ray fluorescence

of untreated rice husk columns with an average particle size of 780 μm and 510 μm from an initial concentration of 100 μg/L at a flow rate of 6.7 and 1.7 mL/min at pH of 6.5 and 6, respectively.

Industrial by-products/wastes such as lignite, peat, chars and bone char have received increasing attention in wastewater treatment. Red mud is a low-cost waste material formed during the production of alumina when bauxite ore is subjected to caustic leaching. Brunori et al. (2005) utilized red mud for treatment of contaminated waters and soils. Treated mud exhibited a high metal trapping capacity that increased with an increase in adsorbent dose in contact with the solution. Only 35% of the arsenic was removed after 48 h of contact time with an adsorbent dose of 2 g/L, but the percentage significantly increased up to 70% with increased adsorbent dose to 10 g/L.

Industrial by-products thus act as good substitute for activated carbon due to their ease of availability and they are inexpensive (Couillard 1992, 1994; Viraraghavan and Ayyaswami 1987). Sneddon et al. (2005) studied the removal of As (V) using a mixture of synthetic hydroxylapatite and barite or bone char in the concentration range of 4–100 mg/L. Bone char was found to be a very effective adsorbent for As(V) in the pH range of 2–5.

A large volume of granular blast furnace slag has been generated by steel plants that is used as filler or in the production of slag cement. Blast furnace slag has been reported as an effective and economical adsorbent for the removal of aqueous arsenic as reported by Zhang and Itoh (2005) and Ahn et al. (2003). An adsorbent was synthesized for aqueous arsenic removal by loading iron(III) oxide onto melted municipal solid waste incinerator slag. The loading of iron oxide on slag increased the surface area of Fe(III)oxide-loaded melted slag (IOLMS) by 68% compared to FeOOH due to the porous structure formed in IOLMS during the synthesis process.

The removal capacities of IOLMS for As(V) and As(III) were observed to be 2.5 and 3 times of those of amorphous hydrous ferric oxide, respectively. About 15 g of IOLMS can remove 200 mg As(V) from 1 L of aqueous solution that meets the

Table 2.4 Adsorptive removal of arsenic using synthesized/modified adsorbents

Adsorbent used	Initial concentration	Efficiency of the adsorbent	Nature of investigation	References
Fe-Mn oxide-impregnated chitosan	0.233 mg/L	54 mg/g	AAS FT-IR	Qui et al. (2015)
Iron oxide-coated sand	0.200 mg/L	0.08 mg/g		Devi et al. (2014)
Synthetic siderite	10 mg/L	10.0 mg/g	SEM EDAX FT-IR	Guo et al.(2011)
Bauxite	1 mg/L	95%	TEM SEM BET	
α-Fe_2O_3 nanoparticles	120 mg/L	95 mg/g	FT-IR SEM	Tang et al.(2011)
Iron-zirconium binary oxide	20 mg/L	120 mg/g	XRD FT-IR	Ren et al.(2011)
α-Fe_2O_3-impregnated chitosan beads	50 mg/L	9.3 mg/g	XRD SEM BET	Liu et al. (2011)
Surfactant (OTMA BDMA DODMA)-modified bentonite	5 mg/L	0.102 mg/g	XRD FT-IR	Jin Su et al. (2011)
Magnetite nanoparticles	1000 mg/g	168 mg/g	SEM EDAX BET	
Phosphorylated orange waste	15 mg/L	0.9 mmol/g	AAS BET-SA	Ghimire et al. (2003)
Portland cement	0.2 mg/L	88.0%	UV/VIS	Kundu et al. (2004)
85% fly ash	100 mg/L	0.45 mg/g	XRD UV-VIS BET	Polowczyk et al. (2007)
Surfactant-modified zeolites	2 mM	0.002 mmol/g	ICP/AES HPLC	Li et al.(2007)
Ferrihydrite (FH)	0.325 mg/L	0.3 mg/g	P-XRD EDAX FT-IR	Jessen et al. (2005)
Iron-modified activated carbon	22 mg/L	30 mg/g	AAS-HV ICP/MS	Chen et al. (2007)
Iron-impregnated mesoporous carbon	0.2–16 mg/L	8.0 mg/g	TEM FT-IR HG/AFS	Masih et al. (2009)
Activated alumina	300 mg/L	80.0%	Titration	Manjare et al. (2005)
Powder activated carbon	5000 mg/L	8.4 mg/g	ICP-OES BET	Tien et al. (2004)
Titania-silica binary oxide-loaded polyacrylonitrile polymer	15 mg/L	0.4 mmol/g	XRD FT-IR TEM TGA	Nilchi et al. (2010)
Iron oxide-coated biomass	0.001 mg/L	0.1 mg/g	GF-AAS	Pokhrel et al. (2008)
Metal(III)-loaded amberlite resins	15 mg/L	484 mmol/kg	XRD BET SEM	Shao et al. (2008)

(continued)

Table 2.4 (continued)

Adsorbent used	Initial concentration	Efficiency of the adsorbent	Nature of investigation	References
Ferric hydroxide microcapsule-loaded alginate beads	100 mg/L	4.8 mg/g	SEM CSV	Sarkar et al. (2010)
Fe-Mn binary oxide	0.133 mM	1.8 mmol/g	XRD XPS BET ICP-OES	Zhanga et al. (2007)
Modified calcined bauxite	1 mg/L	98.8%	XRD EDAX UV/VIS	Zhanga et al. (2007)
Modified calcined bauxite	10,000 mg/L	1.4 mg/g	XRD Zeta studies EDAX UV/VIS	Maji et al. (2007)
Limestone	520 mg/L	0.007 mg/g	AAS SEM	Hossain and Islam (2008)
Aluminium, iron hydroxides	1 mg/L	0.09 mol/mol	XRD XPS	
Mn-substituted iron oxyhydroxide	25 mg/L	4.6 mg/g	XRD BET-SSA FT-IR HG-AAS	Lakshmipathiraj et al. (2006)
Nanocrystalline titanium dioxide	0.300 mg/L	32.4 mg/g	AAS	Bang et al. (2005)
Granular titanium dioxide	0.0267 mM	0.1 mmol/g	GF-AAS	Bang et al. (2005)
Iron hydroxide-coated alumina	1 mM	0.1 mmol/g	BET-SSA GF-AAS	Hlavay and Polyak (2005)
Activated alumina and carbon	300 mg/L	80%	Titration	Manjare et al. (2005)
Biogenic manganese oxides	5 mg/L	0.1 mg/g	BET-SSA GF-AAS	Katsoyiannis et al. (2004)
Goethite	0.10 mM	1.4 μmol/mg	TGA DSC BET	Luxton et al. (2006)
Hybrid adsorbents	1 mg/L	95%	UV/VIS	Nemade et al. (2009a, b)
Basic yttrium carbonate	5–0.2 mmol/L	305.8 mg/g		Wasey et al. (1996)

Note: *AAS* atomic absorption spectroscopy, *FT-IR* Fourier Transform-InfraRed; *SEM* scanning electron microscopy, *EDAX* energy dispersive X-ray analysis, *XRD* X-ray diffraction, *ICP-OES* inductively coupled plasma-optical emission spectrometry, *TEM* transmission electron microscopy, *BET-SSA* Brunauer-Emmett-Teller-specific surface area, *GF/AAS* graphite furnace-atomic absorption spectroscopy, *HPLC* high-performance liquid chromatography, *DSC* differential scanning calorimetry, *XRFS* X-ray fluorescence, *UV-VIS* ultraviolet-visible spectroscopy metal ion concentrations allowed by regulations for industrial wastewater discharge. On the other hand, 65 g of IOLMS was necessary to remove As(III) from 1 L solution to meet the permissible limit. The interactions involved in the removal of arsenic using IOLMS are affinity adsorption that depends on the surface area of IOLMS, the reaction with iron oxides that depends on the existing forms of arsenic species and the reaction with calcium and other metallic elements initially contained in the slag.

The interaction between metal ions and the adsorbent depends on the pH of the solution since the dominant arsenic species {As(V)} in the pH range of 2–7 is H_2AsO_4. Hence the following reaction occurs for the removal of arsenic:

$$\mathrm{FeOOH} + 3H_2\mathrm{AsO_4}^- + 3\mathrm{H}^+ \leftrightarrow \mathrm{Fe}(H_2\mathrm{AsO_4})_3 + 2H_2O \tag{2.1}$$

The coagulation of Ca^{2+} is involved in the removal of As(III) at pH 10 wherein the anionic $H_2AsO_3^-$ predominates. This leads to the possibility of formation of $Ca(H_2AsO_3)_2 \cdot nH_2O$ in the leachate. If the pH of solution increases, only small amounts of Ca^{2+} could be leached, while at $pH < 9$, H_3AsO_3 could not react with Ca^{2+}.

Efforts have been made to utilize fly ash as an adsorbent since the major chemical constituent of fly ash is aluminosilicate. Fly ash is produced as a by-product by combustion of coal in thermal power plants. The disposal of fly ash requires large disposal sites, while its applications have been limited to the production of cement brick and roadbeds. Gupta et al. (2005) report the use of bottom ash as an adsorbent. The kinetic and equilibrium studies performed by Rahman (2004) to evaluate the As(V) removal efficiency using lignite-based fly ash show the metal ion removal at pH 4 as significantly higher than that at pH 7 or 10. Maple wood ash without any chemical treatment was also utilized to remediate As(III) and As(V) from contaminated aqueous streams in low concentrations. Static tests removed almost 80% of arsenic, while the arsenic concentration was reduced from 500 to <5 ppb in dynamic column experiments.

Other aluminosilicates that can be used as adsorbent are clay minerals. These are hydrated aluminosilicates (sometimes with minor amounts of iron magnesium and other cations) and are widespread and abundant in aquatic and terrestrial environments. The structure of clays forms flat hexagonal sheet-like micas. Finely divided clay minerals and oxides exhibit large surface areas. Clay minerals and oxides can adsorb cationic, anionic and neutral metal species. Their sorption capacities, cation- and anion-exchange properties and binding energies vary widely. The investigations of Dousova et al. (2006) and Anjum et al. (2011) show adsorption of arsenic on clay minerals including natural metakaolin, natural clinoptilolite-rich mineral and montmorillonite in both untreated and Fe-treated forms. The studies of Anjum et al. (2011) show the adsorption capacity of cetylpyridinium chloride-modified montmorillonite to be 90% from an initial concentration of 100 mg/L. The lowest level of As(III) that could be extracted was found to be 0.4 mg/L, whereas another

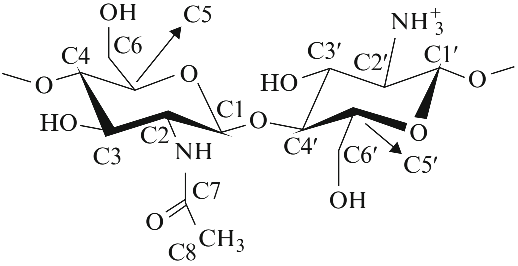

Fig. 2.7 Chemical structure of chitosan

research by Anjum et al. (2013) reports the lowest detection limit as 0.04 mg/L using chitosan-modified montmorillonite. This is due to a large positively charged organoclay surface which facilitates stronger interactions between the adsorbent and the adsorbate, thereby leading to a higher removal capacity of As(III). The sorption capacity of Fe-treated sorbents was 20 mg/g that increased significantly as compared to untreated material (from about 0.5 mg/g) that represented more than 95% of total arsenic removal.

Chitin is the most widely occurring natural carbohydrate polymer next to cellulose. It is a long unbranched polysaccharide derivative of cellulose where the C_2 hydroxyl group has been replaced by the acetyl-amino group – $NHCOCH_3$. Chitin is found in the exoskeleton of *Crustacea*, shellfish, shrimp, crabs and insects. 2-Deoxy-2(acetyl-amino) glucose is the primary unit in the polymer chain. These units are linked by β $(1 \rightarrow 4)$ glycosidic bonds forming long linear chains with degrees of polymerization from 2000 to 4000. Chitosan as shown in Fig. 2.7 is derived from chitin by deacetylation of chitin using concentrated alkali at high temperature. Chitin and chitosan are excellent natural adsorbents that possess high selectivities due to large numbers of hydroxyl and amino groups. These give chitosan a high hydrophilicity: the primary amino groups provide high reactivity or polymer chains of chitosan provide suitable configurations for efficient complexation with metal ions.

The adsorption of arsenic on chitosan, chitin and biomass from *Rhizopus oryzae* was studied by Mcafee et al. (2001). The immobilized biomass offered an outstanding capacity of 0.13 μ equivalents of arsenic per gram at pH 7.

The study by Anjum et al. (2013) shows sorptive removal of As(III) by chitosan-montmorillonite (MMT) composites (in the form of powder and beads). The maximum As(III) sorption capacity of 48.7 mg/g (achieved within 10 min of contact time) was obtained using chitosan-MMT beads in the pH range of drinking water (6–8) at 298 K. The biocomposites show a comparable high sorption capacity with detection and estimation of As(III) from 0.004 (4 ppb) to 100 μg/ml (100 ppm) of aqueous solution. The analyte was found to undergo instantaneous adsorption onto the surfaces as well as surface complexation that further enhanced the adsorption capacity of the analyte onto the sorbents as suggested by kinetic studies as depicted in Fig. 2.8.

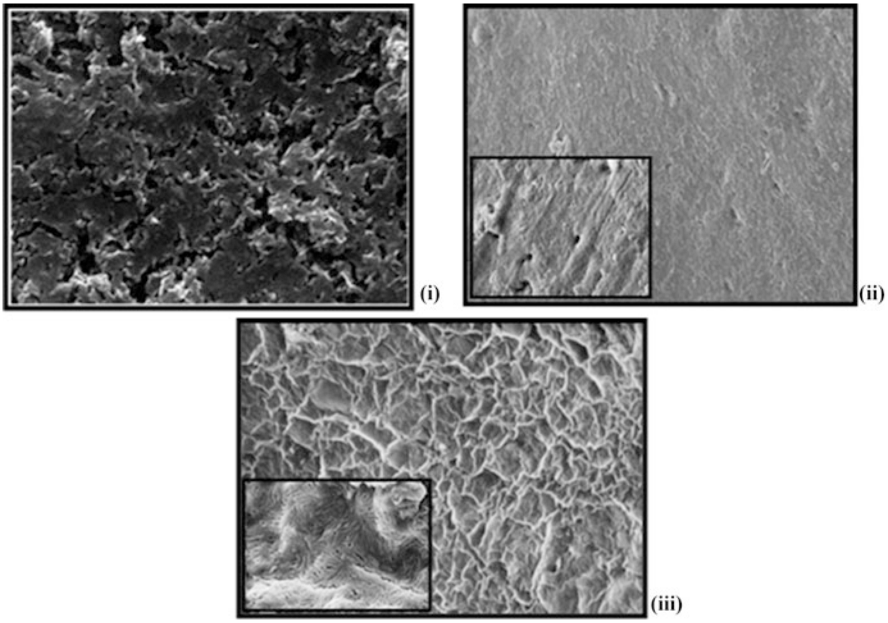

Fig. 2.8 Scanning electron microscopic analysis of (**a**) chitosan-montmorillonite bead (CHMB), (**b**) chitosan bead (CHB), and (**c**) chitosan-montmorillonite composites (CHI-MMT)

The FT-IR-ATR analysis of the adsorbents after As(III) adsorption also supported arsenic sorption and indicated surface complexation between –OH, −NH sites and As(III), respectively, rather than solid-phase precipitation that might generate a large amount of sludge.

2.3.2 *Adsorbents Used for Removal of Antimony*

Antimony has been used by human cultures since the Early Bronze Age. Nriagu (2005) reports that the excavations at Tello in Ancient Chaldea in the far south-eastern corner of Mesopotamia found fragments of an antimony base that dates back to 4000 B.C. Alchemists and quacks have used antimony compounds in medicine, veterinary and cosmetics. It was prescribed in the past as the universal remedy for syphilis, chest pains, the plague, melancholy and especially for fever.

Bowen (1979) reports the concentrations of antimony in groundwater and surface water normally range from 0.1 to 0.2 μg/L. But unfortunately only very few sorption studies of antimony using natural sorbents have been reported.

Sb(III) and Sb(V) bind strongly to hydroxides of Fe and Mn and only weakly to clay minerals (Blay 2000). Extended X-ray adsorption fine structure (EXAFS) measurements of soils from shooting ranges provide evidence for a strong preference of antimony binding to Fe hydroxides. However, the binding mechanism is still unclear.

The observed adsorption capacities for the removal of antimony using various sorbents are summarized in Tables 2.5 and 2.6, respectively.

The surface coverage and pH have a strong influence on the removal of Sb(III) and Sb(V) using iron hydroxides (Blay 2000; Enders and Jekel 1996; Ambe 1987;

Table 2.5 Adsorptive removal of antimony using natural adsorbents

Adsorbent used	Initial concentration	Efficiency of the adsorbent	Nature of investigation	References
Brown algae	100 mg/L	5.4 mg/g	AAS, FT-IR	Ungureanu et al. (2015)
Hematite-modified nanoparticles	0.11 mg/L	95%	XRD, TEM	Shan et al. (2014)
Bentonite	1 mg/L	90%	HPLC H-GAAS BET	Xi et al. (2011)
Bayoxide	0.1 mg/L	95%		Ilavský et al. (2015)
Sodium montmorillonite	0.05 mol/L	0.0003 mol/g	BET GF-AAS ICP	Zhao et al. (2010)
Diatomite	10 mg/L	35.2 mg/g	BET GF-AAS	Ahmet Sarı et al. (2010)
Zero-valent iron	2 mg/L	1.6 μg/g	AAS	
Goethite	2–127 μM	180 μmol/g	HPLC ICP/AES	Leuz et al. (2006)
Brown forest soil	500 mg/L	0.6 mg/kg	XRD ICP/AES	Manaka (2006)
Manganite	0.13 mmol/L	56.5 mg/g	AAS ICP/AES	Filella et al. (2002)
Goethite	1.34 mM	270 mol/g	HPLC HG-AAS	Leuz et al. (2006)
Cerium zirconium hydrous oxides	100 mg/L	98%	AAS	Eva Mištová et al. (2009)
Magnetite	130 μM	56.5 mg/g	BET-SA GF-AAS	Filella et al. (2002)
Hydroxide-type adsorbents	20 mg/L	45 mg/g	AAS FT-IR	Fujita et al. (2006)
Weakly basic ion exchanger	8 μmol/L	0.008 mM	ICP/AE titration	Mercy and Wolfgang (2006)
Rice husks	1.92×10^{-5} M	91%	Radio trace	Khalid et al. (2000)
Zero-valent iron	2 mg/L	1.6 μg/g	AAS	
Alum and ferric salt	0.05 mg/L	90%	HG/AFS	Guo et al. (2009)

(continued)

Table 2.5 (continued)

Adsorbent used	Initial concentration	Efficiency of the adsorbent	Nature of investigation	References
Hydroxyapatite	0.05 mg/L	98%	BET GF-AAS ICP	Leyva et al. (2001)
Olivine	0.100 mM	90%	ICP CHN	
Kaolinite	1 mg/L	27.1%	HG/AFS UV-VIS	Xi et al. (2010)
Silene vulgaris		51.7 mg/kg	HG-AAS	Baroni et al. (2000)

Note: *AAS* atomic absorption spectroscopy, *FT-IR* Fourier Transform-InfraRed, *SEM* scanning electron microscopy, *EDAX* energy dispersive X-ray analysis, *XRD* X-ray diffraction, *ICP-OES* inductively coupled plasma-optical emission spectrometry, *TEM* transmission electron microscopy, *BET-SSA* Brunauer-Emmett-Teller-specific surface area, *GF/AAS* graphite furnace-atomic absorption spectroscopy, *HPLC* high-performance liquid chromatography, *DSC* differential scanning calorimetry, *XRFS* X-ray fluorescence

Thanabalasingam and Pickering 1990). The maximum sorption of Sb(V) on Fe hydroxides was reported at low pH values and extended up to pH 7 at low surface coverage. The adsorption is pH dependant in the absence of organic ligands, namely, tartrate and acetate. This indicates that Sb(III) strongly adsorbs in the pH range 6–10 from an initial concentration of 41 μM.

The mineral surfaces in aqueous systems not only bind metal ions, but can also accelerate oxygenation of Fe(II), Mn(II) and Mn(V) (Wehrli and Stumm 1988). The metal ions bind to oxygen donor ligands of the surface, forming an inner-sphere coordination that has a similar effect as hydrolysis for homogeneous reactions. The adsorption capacity of Sb(V) using goethite was above 96% in the presence of ionic strengths of 0.01 M and 0.1 M between pH 3 and 6, respectively. The adsorption of Sb(V) decreased at pH values of 6.8 and 6.1 at an ionic strength of 0.01 M and 0.1 M, respectively. The EXAFS spectra of goethite after metal ion adsorption show that a Sb(V) octahedron [$Sb(OH)_6^-$] shares an edge with an $Fe(OH)_6$ octahedron and forms an edge-sharing inner-sphere sorption complex at the surface of goethite. The influence of ionic strength on the sorption of Sb(V) was strong above pH 6. This resulted in a lower adsorption of Sb(V) at higher ionic strength. On the other hand, the maximum adsorption capacity of diatomite reported by Sari et al. (2010) for Sb(III) was found to be 35.2 mg/g at pH 6. The adsorption of Sb(III) in the presence of 0.001 M $NaNO_3$ at pH 6 was 68%. If the ionic strength was changed to 0.01 and 0.1 M $NaNO_3$, then the adsorption efficiency decreased to 56% and 48%, respectively, at the same pH. The calculated mean free energy was found to be 7.32 kJ/mol indicating physical adsorption of Sb(III). The investigations for reusability of diatomite show the highest desorption efficiency of 94% using 0.5 M HCl, whereas a decrease of 10% in desorption yield and about 3% adsorption yield was observed after ten adsorption/desorption process cycles due to high stability of

Table 2.6 Adsorptive removal of antimony using synthesized/modified adsorbents

Adsorbent used	Initial concentration	Efficiency of adsorbent	Nature of investigation	References
ZSVI zeolite	100 mg/L	80%	XRD, XPS	Zhou et al. (2015)
$FeCl_3$-modified activated carbon	0.02 mol/L	96.4%	BET	Yu et al. (2014)
Surfactant-modified montmorillonite	100 mg/L	99%	XRD FT-IR	Anjum and Datta (2012)
Zero-valent iron	2 mg/L	0.0016 mg/g	AAS	Tomáš Klimko et al. (2011)
Soil and allophane from hexamethylenetetramine silicic acid	40 mg/L	0.8 mg/g	XRD XRF ICP/MS	Takahash et al. (2010)
Brown forest soil	500 mg/L	0.0006 mg/g	XRD ICP/AES	Manaka (2006)
Manganite	0.13 mmol/L	56.5 mg/g	AAS ICP/AES	Filella et al. (2002)
Bayoxide E33	0.06 mg/L	0.085 mg/g	AAS	Ilavsky (2008)
Goethite	1.34 mM	270 mol/g	HPLC HG-AAS	Leuz et al. (2006)
Cerium and zirconium hydrous oxides	5 mg/L	98%	AAS ICP/AES	Eva Mištová et al. (2009)
Zr(IV)-loaded SOW		114.4 mg/g	FT-IR AAS	Biswas et al. (2009)
Fe(III)-loaded SOW		136.4 mg/g	FT-IR AAS	Biswas et al. (2009)
Chemically bonded adsorbent			FT-IR AAS	Deorkar and Tavlarides (1997)
Amorphous iron and Mn oxyhydroxide	5–20 mg/L	70 mg/g	ACSV	Nelson Belzile et al. (2001)
Magnetite	0.13 mM	56.5 mg/g	BET GF-AAS	Filella et al. (2002)
Hydroxide-type adsorbents	20 mg/L	45 mg/g	AAS FT-IR	Toyohisa Fujita et al. (2006)
Hydrous oxide of Fe		12.1 mg/g	FT-IR AAS	Thanabalasingam and Pickering (1990)
Goethite (α-FeOOH)		61.2	FT-IR AAS	Watkins et al. (2006)
Hydrous oxide of Mn	0.027 mM	17.0 mg/g	ASV	Thanabalasingam and Pickering (1990)
Alum and ferric salt	0.05 mg/L	90%	HG/AFS	Guo et al. (2009)
Pyrrolidine dithiocarbamate	2.5 M	98%	Radiotracer	Sun and Yang (1999)
Diatomite	10 mg/L	35.2 mg/g	BET-SSA GF-AAS	Ahmet Sarı et al. (2010)

diatomite. The calculated thermodynamic parameters show adsorption of Sb(III) onto diatomite as feasible spontaneous and exothermic under the experimental conditions studied.

2.3.3 Adsorbents Used for Removal of Mercury

Chemical reduction by $SnCl_2$ is widely used in mercury analysis in which Hg(II) is reduced to gaseous mercury Hg(0), which is then detected and quantified by methods such as Cold Vapor Atomic Fluorescence Spectrometry (CVAFS). Using $SnCl_2$ to remove Hg(II) (especially trace amounts of mercury) from wastewater was first conceived by Southworth (1996). Field tests demonstrated that stannous tin (Sn^{2+}) was capable of converting dissolved Hg(II) to dissolved elemental mercury Hg(0) in one of the outfalls (Outfall 51) within the Y-12 complex. The study shows that (1) about four to five times more stoichiometrical Sn^{2+} than Hg(II) (Sn/Hg ratio ~ 5) was required to convert the available inorganic mercury to Hg(0), indicating favourable reduction of Hg(II) by $SnCl_2$, given the wastewater chemistry of Outfall 51, and (2) an air/liquid ratio of 20 was sufficient to strip all the resulting Hg(0). The study also indicated that the same chemical reduction might be applied to convert Hg(II) to Hg(0) in the storm drain discharge at Outfall 200 after removal of residual chlorine (Southworth 1997).

The reported adsorption capacities for the removal of mercury using various synthesized sorbents are summarized in Table 2.7. Research was conducted upon the substitution of various functional groups by organic acids, amine bases and sulphur compounds onto the chitosan for Hg(II) adsorption. Recent researches by Peniche et al. (1992) report the effectiveness of chitosan, chitin and crab shell for the chelation of heavy metal ions as shown in Fig. 2.9.

The polyaminated highly porous chitosan beads (PEI-CS) prepared by crosslinking of chitosan beads followed by reaction with EPI and polyethylenimine and the use of N-(2-pyridylmethyl) chitosan (PMC), N-(2-thienylmethyl)chitosan (TMC) and N-[3-(methylthio) propyl]chitosan (MTPC), TMC and MTPC containing sulphur presented higher selectivity to Hg(II) ions than PMC attributable to the fact that Hg(II) is a soft acid that prefers to associate with soft ligand atoms on the basis of the hard and soft (Lewis) acids and bases concept. MTPC shows a higher Hg(II) adsorption capacity (421.3 mg/g) due to the higher coordination ability of the thioether group than the thienyl group and to the existence of a propyl chain spacer unit which would allow for better flexibility of the main ligating atom (the sulphur atom). The adsorption of metal ion on polyaminated highly porous chitosan chelating resin was reported by Kawamura.

Dias et al. (2007) show Hg(II) can be sorbed by some of the reported low-cost adsorbents such as inorganic materials (including zeolites, clay minerals, puzzolanes, iron oxides); industrial wastes generated as by-products (such as lignin, iron (III)hydroxide and red mud); low-rank coal lignite, fly ash and coal; agricultural wastes – natural/chemically modified (such as rice bran, rice husk, wheat bran,

Table 2.7 Adsorptive removal of mercury using synthesized adsorbents

Adsorbent used	Efficiency of the adsorbent	References
Aluminosilicate sieve from fly ash	20 mg/g	Liu et al. (2013)
Activated sludge treated with NaOH	19.3 mg/g	Geetha et al.(2013)
Egyptian mandarin peel	34.8 mg/g	Husein (2013)
Coal ash	90%	Abdelhadi et al. (2011)
Sewage sludge activated with $ZnCl_2$	137.2 mg/g	Otero et al. (2009)
Activated carbon	138 mg/g	McKay et al. (1985)
Polymerization of calix	74.2 mg/g	Tabacki and Yilmaz (2008)
Chitosan immobilized in polyvinyl alcohol	1895.7 mg/g	Son et al. (2004)
2-Mercaptobenzothiazole-treated clay	2.7 mg/g	Dias et al. (1995)
Mesoporous silica-coated magnetic particles	14 mg/g	Dong et al. (2008)
Dithiocarbamate-anchored polymer/ organosmectite composites	157 mg/g	Say et al. (2008)
Polymer/organosmectite composites	214 mg/g	Say et al. (2008)
Fe(III)/Cr(III) waste industrial product	37.3 mg/g	Namasivayam and Senthilkumar (1997)
Activated carbon from fertilizer slurry	560 mg/g	Srivastava et al. (1989)
Chitosan-coated magnetite	99%	Rahbar et al. (2014)
PPN-6 functionalized polymer	99%	Li et al. (2014)
Cation-exchange resin of carboxyl banana	90.8 mg/g	Anirudhan et al. (2002)
Chemically treated sawdust (*Acacia arabica*)	20.6 mg/g	Meena et al. (2008)
Polyacrylamide grafted on banana stalk	138 mg/g	Shibi and Anirudhan (2002)
Used tyre rubber	14.6 mg/g	Meng et al. (1998)
Bicarbonate-treated peanut hull carbon	109.8 mg/g	Namasivayam and Periasamy (1993)
Formaldehyde polymerized sawdust	38.8 mg/g	Raji and Anirudhan (1996)
Photofilm industrial waste sludge	11.7 mg/g	Selvaraj et al.(1998)
From furfural	174 mg/g	Yardim et al. (2003)

wheat husk, sawdust of various plants, bark of the trees, groundnut, hazelnut and coconut shells, cottonseed hulls, waste tea leaves, maize corncob, sugarcane bagasse, apple, banana and orange peels, soybean hulls, grape stalks, sunflower stalks and coffee beans); and activated carbon (AC) prepared from waste materials (agriculture and wood industry, industrial activities and municipal waste). AC is an efficient adsorbent to remove many pollutants from aqueous solutions, but its large-scale production is limited by high production costs. Anoop and Anirudhan (2002) states the removal of mercury (II) from aqueous solutions and chlor-alkali industry effluent by steam activated and sulphurised activated carbons prepared from bagasse pith. Chemically modified wastes enhance the adsorption of heavy metal ions, but at the same time, the cost of the chemicals used in the treatments may increase the cost of the low-cost adsorbents. The use of low-cost adsorbents for heavy metal removal from solution was reviewed by Babel and Kurniawan (2003a, b),

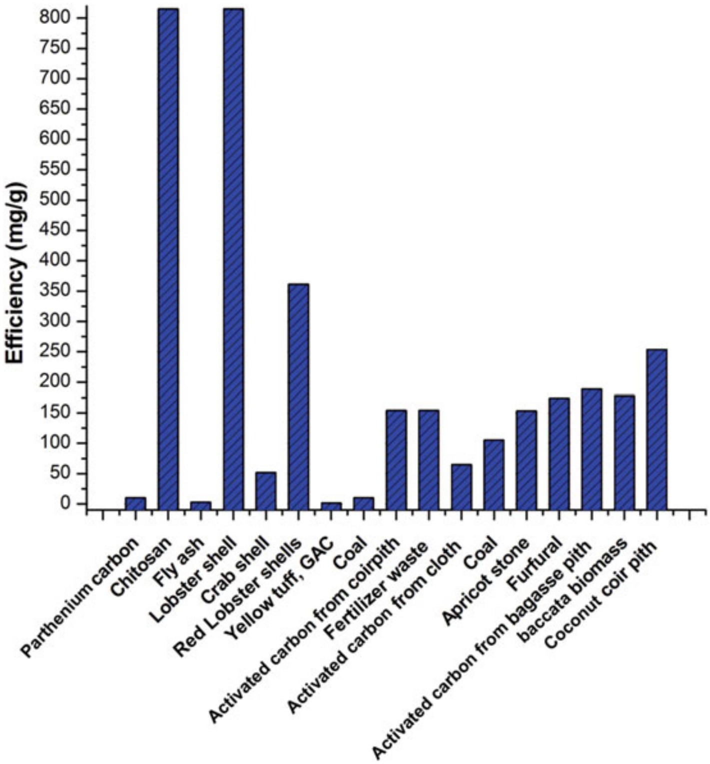

Fig. 2.9 Adsorptive removal of mercury that shows maximum removal efficiency by chitosan and lobster shell. [*Parthenium* carbon (Kadirvelu et al. 2001); chitosan (McKay et al. 1989); fly ash (Sen and Arnab 1987); Lobster shell (Nadeem et al. 2009); crab shell (Peniche Covas et al. 1992); red lobster shells (Taboada et al. 2001); char pozzolana yellow tuff GAC (Di Natale et al. 2006); coal (Karthikeyan and Chaudhuri 1986); activated carbon from coir pith (Namasivayam and Sangeetha 2006); activated carbon from fertilizer waste (Mohan et al. 2001); activated carbon from cloth (Babic et al. 2002); activated carbon from biomass and coal – coals apricot stones furfural (Ekinci et al. 2002); activated carbon from bagasse pith (Krishnan and Anirudhan 2002); marine macroalga *Cystoseira baccata* biomass (Herrero et al. 2005); polyacrylamide-grafted coconut coir pith (Anirudhan and Unnithan 2007; Anirudhan et al. 2008)]

the use of waste materials for activated carbon preparation by Dias et al. (2011), the use of chemically modified plant wastes as adsorbents by Wan Ngah and Hanafiah (2008) and the use of agricultural waste material by Sud et al. (2008).

2.3.4 Adsorbents Used for Removal of Cadmium

The conventional techniques for remediation of cadmium in water have some inherent limitations, such as low efficiency, sensitive operation conditions, production of secondary sludge and costly for their disposal. Thus, numerous adsorbents have been used for the removal of cadmium from water. Balkaya and Cesur (2008) and Ngah and Hanafiah (2008) have reported many low-cost adsorbents obtained from plants for the removal of cadmium. The chemical treatment of these adsorbents has been widely discussed. Chemically modified plant wastes were found to have higher adsorption capacities than unmodified forms possibly due to a higher number of active binding sites, better ion-exchange properties and formation of new functional groups. The modification of rice husk with sodium hydroxide results in an almost double of adsorption. Özer et al. (1999) found that wheat bran had a much higher surface area when treated with sulphuric acid. Hence, the adsorption capacity of wheat brans changed by increasing the conversion of macropores to micropores.

According to Ngah and Hanafiah (2008), the highest adsorption capacity for cadmium was observed to be 313 mg/g using triethylenediamine-treated sugarcane bagasse. The adsorbent consists of increased nucleophilic sites (amide groups) due to chemical modification by triethylenetetramine. The amide group is a result of the chemical reaction between the carboxylic acid group (which was originally the hydroxyl group in sugarcane and converted to carboxylic group by using succinic anhydride) and an amine group. Pretreating sugarcane bagasse with methanol instead of triethylenediamine did not show a good adsorption of cadmium, since methanol acts as an extracting agent for the phenolic groups found in the sugarcane bagasse which means less binding sites, although Ibrahim et al. (2006) considered methanol as a washing agent only.

Activated carbon prepared from various raw materials with high carbonaceous materials including wood, sawdust, coconut shell, coir pith, bone char, nut shells, almond shells, and peanut husks (Rao et al. 2009; Cheung et al. 2001; Ricordel et al. 2001; Ferro-Garcia et al. 1988), has been used for the removal of Cd(II). The activation of carbon can be achieved by thermal decomposition in a high-temperature oxidation or low-temperature chemical dehydration reaction. The adsorption capacity of activated carbon was improved by treating with sulphur (Gomez-serrano et al. 1998), sulphur dioxide (Macías-García et al. 2003), surfactant (Nadeem et al. 2009) or electrochemical oxidation (Rangel-Mendez et al. 2000). Activation was also carried out using $ZnCl_2$ (Kula et al. 2008). The studies revealed that the adsorption occurred through a film diffusion mechanism and the adsorption efficiency for cadmium is higher than that of zinc.

For adsorptive removal of cadmium, agricultural wastes, industrial wastes, low-grade ores, clays and low-cost synthetic oxides/hydroxides such as iron/manganese/aluminium have been used. Some of the low-cost adsorbents with high loading capacities of more than 90 mg/g that have been used for remediation of cadmium are mesoporous silica, mesoporous silicate, broad bean peel, fig leaves, kraft lignin, *Platanus orientalis,* rice husk, modified sugarcane bagasse, modified wheat bran and baker's yeast. Karnitz et al. (2006) show adsorption of metal ions from aqueous single metal solution by chemically modified sugarcane bagasse.

Hydrogels have the capacity to expand their volumes due to their high swelling in water. Hence, they are widely used in the purification of wastewater. Kesenci et al. (2002) prepared poly(ethyleneglycol dimethacrylate-coacrylamide) hydrogel beads with adsorption efficiencies of heavy metals in the order Pb(II) $>$ Cd(II) $>$ Hg(II).

The metal ion removal is governed by the water diffusion into the hydrogel carrying the heavy metals inside, especially in the absence of strong binding sites. The maximum binding capacity increases with an increase in pH to more than 6. The observed adsorption capacities for the adsorption of cadmium using various sorbents are summarized in Tables 2.8 and 2.9, respectively.

The adsorption behaviour of hazelnut shell and hazelnut shell ash as a function of equilibrium time depends on the amount of adsorbent, concentration, pH and

Table 2.8 Adsorptive removal of cadmium using natural adsorbents

Adsorbent used	Initial concentration	Efficiency of the adsorbent	Nature of investigation	References
Luffa cylindrica	100 mg/L	6.7 mg/g		Shahidi et al. (2015)
Chromite mine overburden		22.4 mg/g		Mohapatra and Anand (2007a) and Mohapatra et al. (2009c)
Treated fly ash		14.3 mg/g	XRD EDAX	Chaiyasith et al. (2006)
Iron ore slime		34.7 mg/g		Mohapatra and Anand (2007b)
Manganese nodule residue	100 mg/L	47.6 mg/g		Agarwal and Sahu (2006)
Sugarcane bagasse modified with sodium bicarbonate		189 mg /g	AAS ICP/AES	Ngah and Hanafiah (2008)
Sugarcane bagasse modified with ethylenediamine		313 mg/g	Elemental Analysis FT-IR	Junior et al. (2006)
Sugarcane bagasse modified with methanol		6.7 mg/g	FT-IR	Ibrahim et al. (2006)
Triethylenetetramine m ethanol		7 mg/g	XRD ICP/AES	Ngah and Hanafiah (2008)
Lime-preconditioned phosphogypsum	50 mg/L	132 mg/g	AAS	Balkaya and Cesur (2008)
Aluminium oxide	30 mg/L	127 mg /g	AAS BET-SA	Minamisawa et al. (2005)
Nanoscale diboron/ titanium dioxide	0.1 mg/L	> 95%	ASV	Kalfa et al. (2009)
TiO_2-SiO_2	5 mg/L	≈100%	BET-SA GF-AAS	Ismail et al. (2008)
Amino functional mesoporous silica	100 mg/L	<80%	AAS FT-IR	Aguado et al. (2009)
Humic acid-coated Fe_3O_4 nanoparticles	≈1 mg/L	>91%	AAS	Liu et al. (2008)
ZrPS-001	45 mg/L	~87%	ICP/AE Titration	Zhang et al. (2008)

Table 2.9 Adsorptive removal of cadmium using synthesized/modified adsorbents

Adsorbent used	Initial concentration	Efficiency of the adsorbent	Nature of investigation	References
Chitosan	1000 mg/L	153 mg/g	XRD, FT-IR	Seyedi et al. (2013)
Agricultural waste	125 mg/L	3.9 mg/g		Ali et al. (2013)
Aluminosilicates	*NA*	57.9 mg/g		Rangel et al. (2006)
Calcite	500 μg/L	18.5 mg/g	XRD FT-IR	Yavuz et al. (2000)
Chemically treated clay		12.6 mg/g	XRD FT-IR	Samir (2010)
Low-grade manganese ore	100 mg/L	59.1 mg/g	TEM FT-IR AAS	Mohapatra et al. (2010)
Nalco plant seed	100 mg/L	58.1 mg/g	AAS FT-IR	Mohapatra et al. (2009)
Nickel laterite (high iron)	100 mg/L	13.2 mg/g	AAS FT-IR	Mohapatra and Anand (2007b)
Palygorskite	150 mg/L	4.54 mg/g	AAS	Ayuso and Sanchez (2007)
Perlite		0.64 mg/g		Mathialagan and Viraraghavan (2002)
Red bauxite		38.7 mg/g		Rout et al. (2009)
Sugarcane bagasse		189 mg/g	AAS	Ngah and Hanafiah (2008)
Eucalyptus bark	100 mg/L	15 mg/g	AAS ICP/AES	Ghodbane et al. (2008)
Coffee beans	5 mg/L	>90%	XRD XRF ICP/MS	Minamisawa et al. (2005)
Hazelnut shell ash	30 mg/L	99.1%	AAS	Jamali et al. (2009)
A. rubescens biomass	10 mg/L	97%	HPLC HG-AAS	Sari and Tuzen (2008)
Montmorillonite, kaolin, tobermorite	1–100 mg/L	>80%	ASV	Katsumata et al. (2003)
Red mud	0.002 M	13.0 mg/g	XRD XRF	Gupta and Sharma (2002)
Silica mesoporous		111.3 mg/g	AAS	Ilhan et al. (2004)
Nitric acid-modified corncob		19.3 mg/g	XRD	Ramos et al. (2005)
Sodium hydroxide-modified rice husk		20.24 mg/g	AAS XRD XRF	Kumar and Bandyopadhyay (2006)
Modified cassava tuber bark waste		26.3 mg/g	XRD XRF	Horsfall Jr. et al. (2006)
Sawdust of *Pinus sylvestris*		19.0 mg/g		Costodes et al. (2003)

(continued)

Table 2.9 (continued)

Adsorbent used	Initial concentration	Efficiency of the adsorbent	Nature of investigation	References
Sugar beet pulp		17.2 mg/g		Zacaria et al. (2002)
Teak leaf powder	100 mg/L	86.7%	FT-IR SEM	Rao et al. (2010)

Note: *AAS* atomic absorption spectroscopy, *FT-IR* Fourier Transform-InfraRed, *SEM* scanning electron microscopy, *EDAX* energy dispersive X-ray analysis, *XRD* X-ray diffraction, *ICP-OES* inductively coupled plasma-optical emission spectrometry, *TEM* transmission electron microscopy, *BET-SSA* Brunauer-Emmett-Teller-specific surface area, *GF/AAS* graphite furnace-atomic absorption spectroscopy, *HPLC* high-performance liquid chromatography, *DSC* differential scanning calorimetry, *XRFS* X-ray fluorescence

sorbent particle size using batch system (Jamali et al. 2009). An increase in adsorption efficiency was observed with the increase in pH of the solution. But beyond pH 6, the adsorption efficiency decreased. The maximum adsorption efficiency of 98.2% for hazelnut shell and 99.1% for hazelnut shell ash was attained at pH 6 within a contact time of 3 hours and from an initial concentration of 30 mg/L.

The sorption characteristics of cadmium onto palygorskite as a function of contact time of 0.5–48 h, initial cadmium concentration (5–150 mg/L or 0.044–1.34 mmol/L), ionic strength ([Ca(II)]: 0–0.1 mol/L), pH 3–7 and adsorbent dose of 1–20 g/L were investigated by Ayuso et al. (2007). The equilibrium was attained within 30 min of interaction of adsorbent with cadmium. This process is described by the Langmuir model and gave a maximum Cd sorption of 4.54 mg/g. The sorption decreased with a decrease in solution pH especially at proton concentrations similar to those of cadmium at which competition for the silanol groups on the palygorskite surface appeared to be important. High competing electrolyte concentrations also decreased significantly (close to 60%) the amount of sorbed Cd, suggesting a great contribution of the replacement of exchange cations in this metal removal by palygorskite. The efficiency of the adsorbent was increased to 85–45% using an adsorbent dose of 20 g/L.

Katsumata et al. (2003) investigated removal of Cd(II), Cr(VI), Cu(II) and Pb (II) (initial concentration 1.0 mg/L) from wastewater using montmorillonite, kaolin, tobermorite, magnetite, silica gel and alumina by the column method. The adsorption efficiency of cadmium increased with increase in solution pH. A high removal efficiency of more than 80% was obtained from an initial concentration range of 1–100 mg/L of metal ion. However, with increasing concentration of cadmium ions at more than 100 mg/L, the adsorption efficiency gradually decreased.

Sari and Tuzen (2008) studied the adsorption of cadmium and lead ions using *A. rubescens* biomass from aqueous solution. The sorption capacity for cadmium was observed to be 27.3 mg/g at pH 5 within a contact time of 30 min at 20 °C. With an increase in pH from 2 to 4, the sorption efficiency increased from 35 to 70% for cadmium ions. However, the maximum sorption was found to be 97% at pH 5. Thermodynamic calculations showed that the nature of the sorption of the metal ion was exothermic and spontaneous.

Aguado et al. (2008) used modified oxide sorbent (bound or coated) to remove cadmium ions. Mesoporous silica was functionalized with organic chains containing one, two or three amino groups. The results show that the adsorbent prepared by co-condensation had a negligible metal adsorption capacity, whereas amine-grafted materials adsorb significant amounts ranging from 30 to around 75% of Cd(II) from an initial aqueous solution of 100 mg/L, depending on the amino functional groups present on the sorbent.

2.3.5 Adsorbents Used for Removal of Lead

Lead is introduced to the environment as a consequence of many human activities, such as lead paint production (Mielke 1993), mining (Cotter-Howels and Thornton 1991) and production of agricultural fertilizers, insecticides and pesticides (Ma et al. 1995). Studies have shown that there is a strong correlation between chronic lead exposure to children and impaired cognitive skills (Tong 1998), intellectual impairment, reduced IQ and mental retardation (Nevin 2009). Thus, removal of lead from water and soil will have positive and beneficial implications on the ecosystem, global economy, agriculture and health. Currently, many technologies such as phytoremediation (extraction, stabilization and volatilization) have emerged for the removal of lead from soil (Lone et al. 2008; Chane 1997). The observed adsorption capacities for the adsorption of lead using various sorbents are summarized in Table 2.10.

Annadurai et al. (2002) and Tarley and Arruda (2003) report that the use of some agricultural products, such as sugarcane bagasse, rice husks and coconut husks, has gained attention as biosorbents due to their economic viability and abundance availability from renewable sources.

Transmission electron micrographs of lyophilized *B. longum* 46 and *L. fermentum* ME3 before and after lead binding show the presence of lead on the surface of both strains after binding. Small deposits of lead were also visible inside the bacteria. These deposits were transferred from the bacterial surface during the sample preparation for electron microscopy. Transmission electron micrographs established that lead binding occurred at the surface of the bacterial cells.

Giraldo (2008) and Moreno-Pirajan et al. (2008) used activated carbon from sawdust (ACS) for the removal of lead. The adsorbent showed a sorption capacity of 17.5 mg/g at an initial concentration of 10–100 mg/L. The adsorption efficiency of industrial waste (sludge from blast furnace) investigated by Lopez et al. (1998) shows a sorption capacity of 79.8 mg/g. Vassileva et al. (1996) showed a maximum metal sorption capacity of 10 mg/g at a concentration range of 0.001 to 0.02 mg/L using ceria (CeO_2). Magnetic γ –Fe_2O_3 nanoparticles studied by White et al. (2009) show an adsorption capacity of 15 ± 3 mg/g from a dilute solution of 1 mg/L of metal ion. On the other hand, nanosized magnetite was studied by Yavuz et al. (2000). It shows an adsorption efficiency of more than 90% that forms a dilute solution of 0.1 mg/L. The active sites on adsorption media may show charge over

Table 2.10 Adsorptive removal of lead using natural adsorbents

Adsorbent used	Initial concentration	Efficiency of the adsorbent	References
Activated carbon	200 mg/L	584 mg/g	Yarkandi (2014)
Bentonite	200 mg/L	559 mg/g	Yarkandi (2014)
Instant coffee (IC-S)	211 mg/ L	83.5%	Agwaramgbo et al. (2013)
Coffee bean (CB-S)	225 mg/L	82.4%	Agwaramgbo et al. (2013)
Alginate-SBA-15	200 mg/L	222.2 mg/g	Cheraghali et al. (2013)
Alginate of calcium beads		58.0 mg/g	Zhang et al. (2013)
Tea (tea-S)	44 mg/L	97%	Agwaramgbo et al. (2013)
Fish bone (FB-S)	298 mg/L	77%	Agwaramgbo et al. (2013)
Caffeine (CAF-S)	1263 mg/L	1%	Agwaramgbo et al. (2013)
F. vesiculosus	1–100 mg/L	468.2 mg/g	KatsuMata (2003)
Peach and apricot stones	10 mg/L	93%	Rashed (2006)
Hazelnut shell	1 mM	28.1 mg/g	Pehlivan et al. (2009)
Almond shell	0.1 mM	8.0 mg/g	Pehlivan et al. (2009)
Modified sugarcane bagasse		52.6 mg/g	Dos Santos et al. (2010)
B. lactis Bb12	1.0 mg/L	111 mg/g	Teemu et al. (2008)
B. longum 2C	1.0 mg/L	47 mg/g	Teemu et al. (2008)
B. longum 46	0.10–1.0 mg/L	176 mg/g	Teemu et al. (2008)
L. casei shirota	0.10–1.0 mg/L	98 mg/g	Teemu et al. (2008)
L. fermentum ME3	0.10–1.0 mg/L	136 mg/g	Teemu et al. (2008)
L. rhamnosus GG	1.0 mg/L	107 mg/g	Teemu et al. (2008)
Granular-activated carbon		26.5 mg/g	Dwivedi et al. (2008)
Activated carbon from African palm pit (ACP)		15.2 mg/g	Giraldo and Moreno-Pirajan (2008)
Activated carbon from sugar-cane bagasse (ACB)		13.7 mg/g	Giraldo and Moreno-Pirajan (2008)
Olive stone		5.8 mg/g	Calero et al. (2009)
Activated carbon from coconut (CA)	100 mg/L	4.3 mg/g	Gueu et al. (2007)
Activated carbon from palm tree (GA)	100 mg/L	3.7 mg/g	Gueu et al. (2007)
Tunisian smectite-rich clay		41%	Chaari et al. (2008)
Activated-waste mud (a-WM)	235 ppm	82%	Ozdes et al. (2009)
Zeolite clinoptilolite		1.6 mg/g	Babel and Kurniawan (2003a, b)
Modified zeolite MMZ		123 mg/g	Nah et al. (2006)

(continued)

Table 2.10 (continued)

Adsorbent used	Initial concentration	Efficiency of the adsorbent	References
Clay/poly(methoxyethyl) acrylamide		81 mg/g	Sölenera et al. (2008)
Clay/poly(methoxyethyl) acrylamide		85.6 mg/g	Aklil et al. (2004)
Maize cope and husk		456 mg/g	Igwe et al. (2005)
Ecklonia maxima – marine algae		235 mg/g	Fenga and Aldrich (2004)
Oedogonium species		145 mg/g	Gupta and Rastogi (2008)
ZrPS-001	80 mg/L	>99%	Zhang et al. (2008)

certain pH ranges. This implies that charge behaviour of the contaminant and the adsorbent are equally important to determine the required pH adjustment for the selected treatment application. The adsorbent is selected depending on the oxidation state of the metal ion. The adsorption efficiency of some good adsorbents has been depicted in Fig. 2.10.

Activated coconut shell carbon powder (ACSCP) and activated charcoal powder (ACP) are used as adsorbent for the removal of lead from electrochemical industry effluent as shown by Nishigandha et al. (2015). Baari et al. (2008) studied the removal of Pb(II) using Tunisian smectite-rich clay (sampled in Jebel Aïdoudi in El Hammaarea (meridional Atlas of Tunisia)) in aqueous solution. Four smectite clay samples, untreated clay (UC), hydrochloric activated clay (HAC), sulphuric-activated clay (SAC) and thermic-activated clay (TAC), were used. HAC and SAC samples enhanced the adsorption capacity under the same conditions compared to the untreated clay minerals due to the increased surface area. The removal of Pb(II) by SAC was observed to be very high when compared to HAC because clay minerals are more soluble in sulphuric acid than hydrochloric acid. HAC and SAC removed as much as 50.1 and 65.1% of Pb(II), respectively, whereas UC could remove only 41.3%. The removal of lead by the TAC sample calcined at 100 °C was 54.2%, but the efficiency decreased with increase in temperature. A comparative study between activated carbon and SAC showed that the adsorption capacity of SAC was better than that for activated carbon.

2.3.6 *Adsorbents Used for Removal of Zinc*

The adsorption for the removal of Zn^{2+} includes the use of natural materials such as bagasse, moss, bentonite and mixed mineral; microbial and algal biomass including seaweed, yeast, fungi and bacteria; and industrial and agricultural wastes such as

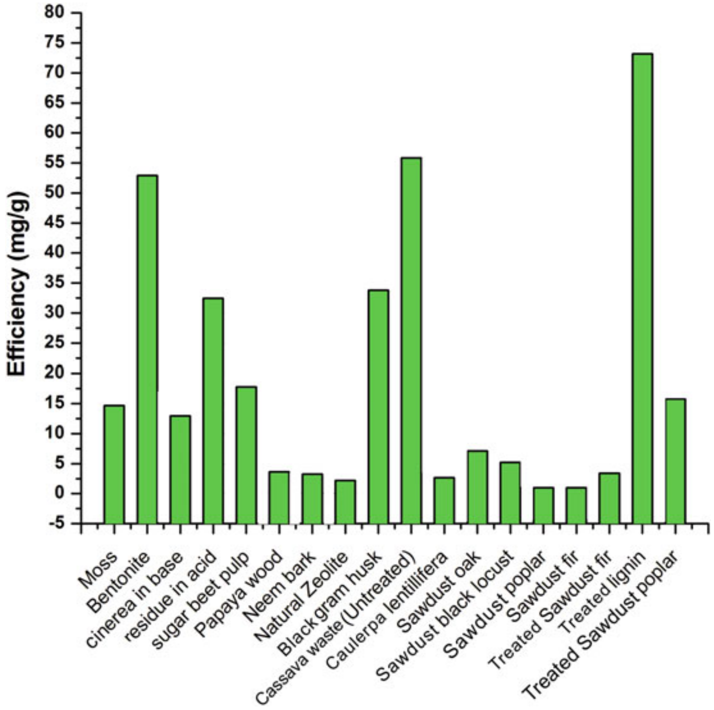

Fig. 2.10 Some adsorbents that show good efficiency of lead removal using treated lignin [Moss (Martins et al. 2004); bentonite (Mellah and Chegrouche 1997); *Botrytis cinerea* (Tunali and Akar 2006); sea nodule residue in acid (Agrawal et al. 2004); sugar beet pulp (Reddad et al. 2002); papaya wood (Saeed et al. 2005a, b); neem bark (Bhattacharya et al. 2006); natural zeolite (Motsi et al. 2009); black gram husk (Saeed et al. 2005); cassava waste (untreated) (Horsfall et al. 2003); *Caulerpa lentillifera* (Pavasant et al. 2006); sawdust oak, sawdust black locust, sawdust poplar, sawdust fir and NaOH-treated sawdust fir (Sciban et al. 2006a, b); HCl + ether + benzene-treated lignin (Srivastava et al. 1994); NaOH-treated sawdust poplar (Sciban et al. 2006a, b)]

corncobs, peanut hulls, hazelnut shells, corn starch, waste tea leaves, sea nodule residue, blast furnace slag, sugar beet pulp, lignite, lignin and powdered waste sludge as listed in Table 2.11. The chemical modification of plant wastes poses several problems such as low adsorption capacity, high chemical oxygen demand (COD), biological chemical demand (BOD) and total organic carbon (TOC) due to the release of soluble organic compounds contained in the plant materials. The increase of the COD, BOD and TOC can cause depletion of the oxygen content in water and can threaten the aquatic life. Thus, according to Gaballah et al. (1997), plant wastes need to be chemically treated or modified before being applied for the decontamination of heavy metals. Also pretreatment of plant wastes can extract soluble organic compounds and enhance the chelating efficiency.

Babel and Kurniawan (2003a, b) state that numerous studies have so far been discussing the importance of low-cost adsorbents in water pollution control, many of them are generally either adsorbate specific (metals, dyes and phenols) or

Table 2.11 Adsorptive removal of zinc using synthesized adsorbents

Adsorbent used	Efficiency of the adsorbent	References
Zero-valent irons	10^{-5} M	Suponik et al. (2015)
Sawdust	90%	Pragati et al. (2015)
Powdered waste sludge	128.8 mg/g	Zwain et al. (2014)
Clarified sludge	168 mg/g	Zwain et al. (2014)
Rice husk ash + coal fly ash + palm oil fuel ash	16.9 mg/g	Zwain and Dahlan (2012)
Dried marine green macroalgae	15.5 mg/g	Saeed et al. (2005)
Sea nodule residue in acid	32.4 mg/g	Agrawal et al. (2004)
H_2O_2-modified powdered waste sludge	168 mg/g	Kargi and Cikla (2006)
Waste-activated sludge	36.9 mg/g	Norton et al. (2004)
Activated alumina	13.6 mg/g	Bhattacharya et al. (2006)
Acid-treated saltbush leaves	32.7 mg/g	Sawalha et al. (2007)
Coal fly ash	6.5–13.3 mg/g	Mohan and Singh (2002)
Fe impregnated fly ash ($FeCl_3$ 30°–60°)	7.5–15.5 mg/g	Banerjee et al. (2003)
Al impregnated fly ash (($Al(NO_3)_2$ 30°–60°)	7.0–15.4 mg/g	Banerjee et al. (2003)
Cassava waste (thioglycolic acid + nitric acid)	559.7 mg/g	Horsfall and Abia (2003)
Acid-modified bagasse	31.1 mg/g	Mohan and Singh (2002)
Formaldehyde-treated sawdust oak	6.1 mg/g	Sciban et al. (2006a, b)
Formaldehyde + NaOH-treated sawdust oak	9.3 mg/g	Sciban et al. (2006a, b)
Formaldehyde-treated sawdust black locust	5.3 mg/g	Sciban et al. (2006a, b)
HCHO + NaOH-treated sawdust black locust	9.0 mg/g	Sciban et al. (2006a, b)

adsorbent specific. Hence, different forms of inexpensive and nonliving plant material have been studied as potential adsorbent, such as black gram husk by Saeed et al. (2005) as shown in Fig. 2.9, eggshell by Park et al. (2007), sugar beet pectin gels by Mata et al. (2009) and citrus peels by Schiewer and Patil (2008).

Adsorption of divalent heavy metal ions, particularly Cu^{+2}, Zn^{+2}, Co^{+2}, Ni^{+2} and Pb^{+2} onto acid- and alkali-treated banana and orange peels was performed by Annadurai et al. (2003). Residues of banana and orange peels are cellulose-based wastes. Hence, they can be processed and converted to be adsorbents, because they have a large surface area, high swelling capacity and excellent mechanical strength. Thus, they are convenient to use and have great potential to adsorb harmful contaminants such as heavy metals. In addition, the acid and alkali solutions used for modification of adsorbents were HNO_3 and NaOH. Generally, the adsorption capacity decreases in the order of $Pb^{2+} > Ni^{2+} > Zn^{2+} > Cu^{2+} > Co^{2+}$ for both adsorbents. Banana peel exhibits a higher maximum adsorption capacity for heavy metals compared to orange peel. The reported maximum adsorption capacities can be summarized as follows: 7.97 (Pb^{2+}), 6.88 (Ni^{2+}), 5.80 (Zn^{2+}), 4.75 (Cu^{2+}) and 2.0 (Co^{2+}) mg/g using banana peel and 7.75 (Pb^{2+}), 6.01 (Ni^{2+}), 5.25 (Zn^{2+}), 3.65 (Cu^{2+}) and 1.82 (Co^{2+}) mg/g using orange peel, respectively. Acid-treated peels showed better adsorption capacities followed by alkali- and water-treated peels. Based on regeneration studies, it was reported that the peels could be used for two regenerations of heavy metal ions removal and recovery.

Rice husk pretreatment can remove hemicellulose, and lignin reduces the cellulose crystallinity and increases the surface area or porosity. In general, unmodified rice husk showed lower adsorption capacities on heavy metal ions than untreated or chemically modified rice husk. It was reported by Kumar and Bandyopadhyay (2006) that rice husk treated with sodium carbonate, sodium hydroxide and epichlorohydrin enhanced the adsorption capacity of heavy metals. Also it was reported that adsorption properties by the base treatment (NaOH) remove base soluble materials from the rice husk surface. Bhattacharya et al. (2006) studied pretreated rice husk ash for the removal of Zn^{2+}. An efficiency of 96.8% of Zn^{2+} removal was obtained at pH 5. The Langmuir and Freundlich adsorption isotherm models were used to represent the experimental data, wherein both models fitted well. The adsorption capacity was obtained as 14.3 mg/g at optimum pH 5.0.

In another study by Montanher et al. (2005), rice bran was evaluated for its potential use as an adsorbent for Cd^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+}. Rice bran adsorbent is able to successfully adsorb the metal ions from aqueous solutions. Maximum efficiency of 72% for Zn^{2+} removal was observed in chloride medium, and 0.1 mol/L NaCl has been used throughout the work. The experimental data were well fitted to the Freundlich equation with good correlation coefficients.

2.4 Conclusion

This chapter shows that adsorption is a very promising and effective technology as a remediation to toxic metals present in groundwater. The technology involves the use of various adsorbents, including natural and chemical/synthesized ones that have effectively removed heavy metals from water. Besides the operating parameters of removal of heavy metal ions from water, the increasing costs and environmental considerations have in recent years led to the use of new low-cost adsorbents derived from renewable resources. Chemical modification of different wastes increases the adsorption capacity, but the technology cost and side pollution must be taken in consideration in order to produce real “low-cost” adsorbents.

The metal ions are attracted and bound to the sorbent due to high affinity through a complex process that depends on ion-exchange chemisorption, complexation, adsorption on the surface and pores, chelation and adsorption by physical forces due to a concentration gradient and diffusion through the biosorbent material. The presence of competitive cations and chelators reduces the metal removal capacity of an adsorbent due to which some adsorbents may show poor adsorption capacity, low efficiency/cost ratio and ineffectiveness for high or very low metal concentration. On the other hand, a decrease in sorbent particle size leads to an increase in the sorption of metal ions. This is overcome by chemical modification of the adsorbent that improves the adsorption capacity of adsorbents due to an increased number of active binding sites, better ion-exchange properties and formation of new functional groups. The initial metal ion concentration, initial solution temperature, solution pH, flow rate, sorbent mass and contact time are known to affect the metal removal efficiency from water. The operating temperature changes the rate of molecular interactions and solubility.

References

Abdelhadi MA, Yoshihiko T, Abdelhadi NA, Matouq M (2011) Utilization of fly ash linear materials as an adsorbent of hazardous chemical compounds. J Sci Res Essays 6 (15):3330–3334. doi:10.5897/SRE11.752

Abollino O, Aceto M, Malandrino M, Sarzanini C, Mentasti E (2003) Adsorption of heavy metals on Na-montmorillonite. Effect of pH and organic substances. Water Res 37:1619–1627. doi:10.1016/S0043-1354(02)00524-9

Adhoum N, Monser L, Bellakhal N, Belgaied JE (2004) Treatment of electroplating wastewater containing Cu^{2+} $Zn^{2+}$and Cr^{6+} by electrocoagulation. J Hazard Mater B 112(3):207–213. doi:10.1016/j.jhazmat.2004.04.018

Agrawal A, Sahu KK (2006) Kinetic and isotherm studies of cadmium adsorption on manganese nodule residue. J Hazard Mater B137:915–924. doi:10.1016/j.jhazmat.2006.03.039

Agrawal A, Sahu KK, Pandey BD (2004) Removal of zinc from aqueous solutions using sea nodule residue. Colloid Surf A Physicochem Eng Aspect 237(1–3):133–140. doi: http://dx.doi.org/10.1016/j.colsurfa.2004.01.034

Aguado J, Arsuaga JM, Arencibia A, Lindo M, Gascón V (2009) Aqueous heavy metals removal by adsorption on amine-functionalized mesoporous silica. J Hazard Mater 163:213–221. doi:10.1016/j.jhazmat.2008.06.080

Agwaramgbo L, Nichole L, Edwards S, Nunez S (2013) Assessing lead removal from contaminated water using solid biomaterials: charcoal coffee tea fishbone and caffeine. J Environ Prot 4:741–745. doi:10.4236/jep.2013.411145

Ahluwalia SS, Goyal D (2007) Microbial and plant derived biomass for removal of heavy metals from wastewater. Bioresour Technol 98(12):2243–2257, https://doi.org/10.1016/j.biortech.2005.12.006

Ahmed MF, Ahuja S, Alauddin M, Hug SJ, Lloyd JR, Pfaff A, Pichler T, Saltikov C, Stute M, Geen VA (2006) Ensuring safe drink. Water Bangladesh. Science 314(5806):1687–1688. doi:10.1126/science.1133146

Ahn JS, Chon CM, Moon HS, Kim KW (2003) Arsenic removal using steel manufacturing by-products as permeable reactive materials in mine tailing containment systems. Water Res 37(10):2478–2488. doi:10.1016/S0043-1354(02)00637-1

Ahsan H, Chen Y, Parvez F, Argos M, Hussain AI, Momotaj H (2006) Health effects of Arsenic Longitudinal Study (HEALS): description of a multidisciplinary epidemiologic investigation. J Expos Sci Environ Epidemiol 16:191–205. doi:10.1038/sj.jea.7500449

Aklil A, Moufliha M, Sebti S (2004) Removal of heavy metal ions from water by using calcined phosphate as a new adsorbent. J Hazard Mater A112:183–190. doi:10.1016/j.jhazmat.2004.05.018

Ali M, Hashimi A, Manar M, Safar A (2013) Removal of cadmium from synthetic water by using agricultural wastes. Acta Technica Corviniensis VI 2:131–138

Ambe S (1987) Adsorption kinetics of antimony(V) ions onto α-Fe_2O_3 surfaces from an aqueous solution. Langmuir 3(4):489–493. doi:10.1021/la00076a009

Anirudhan TS, Unnithan MR (2007) Arsenic(V) removal from aqueous solutions using an anion exchanger derived from coconut coir pith and its recovery. Chemosphere 66(1):60–64. doi:10.1016/j.chemosphere.2006.07.080

Anirudhan TS, Divya L, Ramachandran M (2008) Mercury (II) removal from aqueous solutions and waste waters using a novel cation exchanger derived from coconut coir pith and its recovery. J Hazard Mater 157(2–3):620–627. doi:10.1016/j.jhazmat.2008.01.030

Anjum A, Datta M (2012) Adsorptive removal of antimony (III) using modified montmorillonite: A study on sorption kinetics. J Anal Sci Methods Instr 2:167–175. doi:10.4236/jasmi.2012.23027

Anjum A, Lokeswari P, Kaur M, Datta M (2011) Removal of As (III) from aqueous solutions using Montmorillonite. J Analyt Sci Method Instr 1:25–30. doi:10.4236/jasmi.2011.12004

Anjum A, Seth CK, Datta M (2013) Removal of As^{3+} using chitosan-montmorillonite composite: sorptive equilibrium and kinetics. Adsorpt Sci Technol 31(4):303–324. doi:10.5539/ijc.v7n1p28

Annadurai G, Juang RS, Lee DJ (2003) Adsorption of heavy metals from water using banana and orange peels. Water Sci Technol 47(1):185–190. doi:10.1007/s13204-015-0401-2

Anoop KK, Anirudhan TS (2002) Removal of mercury (II) from aqueous solutions and chlor-alkali industry effluent by steam activated and sulphurised activated carbons prepared from bagasse pith: Kinetics and equilibrium studies. J Hazard Mater 92:161–183. doi:10.1016/S0304-3894(02)00014-6

Ansone L, Klavins M, Viksna A (2013) Arsenic removal using natural biomaterial-based sorbents. Environ Geochem Health 35(5):324–335. doi:10.1007/s10653-013-9546-7

Arslanoglu H, Altundogan HS, Tumen F (2009) Heavy metals binding properties of esterified lemon. J Hazard Mater 164(2):1406–1413. doi:10.1016/j.jhazmat.2008.09.054

Aryal M, Ziagova M, Liakopoulou-Kyriakides M (2010) Study on arsenic biosorption using Fe (III)-treated biomass of *Staphylococcus xylosus*. Chem Eng J 162:175–185. doi:10.11912/jws.3.3.117-131

Aydinalp C, Marinova S (2003) Distribution and forms of heavy metals in some agricultural soils [Letter to the editor]. Polish J Environ Stud 12(5):629–633. doi:10.11912/jws.3.3.117-131

Aylett BJ (1979) The chemistry and bioinorganic chemistry of cadmium. In: Webb M (ed) The chemistry biochemistry and biology of cadmium. Elsevier/North-Holland, Amsterdam, pp 1–44. doi:10.1007/978-1-59259-458-0

Ayuso EI, Garcia-Sanchez A (2007) Removal of cadmium from aqueous solutions by palygorskite. J Hazard Mater 147:594–600. doi:10.1016/j.jhazmat.2007.01.055

Babel S, Kurniawan TA (2003a) Low-cost adsorbents for heavy metals uptake from contaminated water: a review. J Hazard Mater 97(1–3):219–243, https://doi.org/10.1016/S0304-3894(02)00263-7

Babel S, Kurniawan TA (2003b) Various treatment technologies to remove arsenic and mercury from contaminated groundwater: an overview. In: Proceedings of the first international symposium on Southeast Asian Water Environment (ISSAWE-2003) Bangkok, Thailand, pp 433–440

Babic BM, Milonjic SK, Polovina MJ, Cupic S, Kaludjero BV (2002) Adsorption of zinc cadmium and mercury ions from aqueous solutions on an activated carbon cloth. Carbon 40:1109–1115. doi:10.1016/S0008-6223(01)00256-1

Balkaya N, Cesur H (2008) Adsorption of cadmium from aqueous solution by phosphogypsum. Chem Eng J 140:247–254. doi:10.1016/j.cej.2007.10.002

Banerjee SS, Jayaram RV, Joshi MV (2003) Removal of nickel (II) and zinc(II) from wastewater using fly ash and impregnated fly ash. Sep Sci Technol 38(5):1015–1032. doi:10.1081/SS-120018121

Bang SB, Patel M, Lippincott L, Meng XG (2005) Removal of arsenic from groundwater by granular titanium dioxide adsorbent. Chemosphere 60:389–397. doi:10.1016/j.chemosphere.2004.12.008

Barakat MA, Sahiner N (2008) Cationic hydrogels for toxic arsenate removal from aqueous environment. J Environ Manag 88:955–961. doi:10.1016/j.jenvman.2007.05.003

Barnhart J (1997) Occurrences uses and properties of chromium. Regul Toxicol Pharmacol 26(1 Pt 2):S3–S7. doi:10.1006/rtph.1997.1132

Baroni F, Boscagli A, Protano G, Riccobono F (2000) Antimony accumulation in *Achillea ageratum Plantago lanceolata* and *Silene vulgaris* growing in an old Sb-mining area. Environ Pollut 109:347–352. doi:10.1016/S0269-7491(99)00240-7

Belzile N, Chen Y, Wang Z (2001) Oxidation of antimony (III) by amorphous iron and manganese oxyhydroxides. Chem Geol 174:379–387. doi:10.1016/j.chemgeo.2009.01.008

Bhattacharya AK, Mandal SN, Das SK (2006) Adsorption of Zn(II) from aqueous solution by using different adsorbents. Chem Eng J 123(1–2):43–51. doi:10.1016/j.cej.2006.06.012

Bhattacharyya N, Baugh RF, Orvidas L, Barrs D, Bronston LJ, Cass S, Chalian AA, Desmond AL, Earll JM, Fife TD, Fuller DC, Judge JO, Mann NR (2008) Clinical practice guideline: benign paroxysmal positional vertigo. Otolaryngol Head Neck Surg 139(5 Suppl 4):S47–S48

Biswas BK, Inoue J, Inoue K, Ghimirie KD, Harada H, Ohto K, Kawakita H (2007) Adsorptive removal of As(V) and As(III) from water by a Zr(IV)- loaded orange waste gel. J Hazard Mater 154(1–3):1066–1074. doi:10.1016/j.jhazmat.2007.11.030

Biswas BK, Inoue J-I, Inoue K et al (2008) Adsorptive removal of As(V) and As(III) from water by a Zr(IV)- loaded orange waste gel. J Hazard Mater 154(1–3):1066–1074. doi:10.1016/j.jhazmat.2007.11.030

Biswas BK, Inoue J, Kawakita H, Ohto K, Inoue K (2009) Effective removal and recovery of antimony using metal-loaded saponified orange waste. J Hazard Mater 172(2–3):721–728. doi:10.1016/j.jhazmat.2009.07.055

Blacksmith Institute (2010) Blacksmith institute's world's worst pollution problems report, New York, USA

Blay K (2000) Sorption wässriger Antimon-Spezies an bodenbildende Festphasen und Remobilisierung durch natürliche Komplexbildner (Sorption of aqueous Sb species to soil forming minerals and remobilization by natural ligands). Doctoral dissertation, Technical University of Munich, Germany

Boddu VM, Abburi K, Talbott JL, Smith ED, Haasch R (2008) Removal of arsenic (III) and arsenic (V) from aqueous medium using chitosan-coated biosorbent. Water Res 42 (3):633–642. 0043-1354. doi:10.1016/j.watres.2007.08.014

Bowen HJM (1979) Environmental chemistry of the elements. Academic Press, London/New York

Brunori C, Cremisini C, Massanisso P, Pinto V, Torricelli L (2005) Reuse of a treated red mud bauxite waste: studies on environmental compatibility. J Hazard Mater 117(1):55–63. doi:10.1016/j.jhazmat.2004.09.010

Calero M, Hernainz F, Blazquez G, Martín-Lara MA, Tenorio G (2009) Biosorption kinetics of Cd (II) Cr (III) and Pb (II) in aqueous solutions by olive stone Brazilian. J Chem Eng 26:265–273. doi: None

Candinas T et al (1999) Bodenbelastung durch Klärschlamm und andere Dünger. Agrarforschung 6:309–312

Chaari I, Fakhfakh E, Chakroun S, Bouzid J, Boujelben N, Feki M, Rocha F, Jamoussi F (2008) Lead removal from aqueous solutions by a Tunisian smectitic clay. J Hazard Mater 156:545–551. doi:10.1016/j.jhazmat.2007.12.080

Chaiyasith S, Chaiyasith P, Septhum C (2006) Removal of cadmium and nickel from aqueous solution by adsorption onto treated fly ash from Thailand. Int J Sci Technol 11(2):13–20

Chen CC, Chung YC (2006) Arsenic removal using a biopolymer chitosan sorbent. J Environ Sci Health A Tox Hazard Subst Environ Eng 41(4):645–648

Chen W, Parette R, Zou J, Cannon FS, Dempsey BA (2007) Arsenic removal by iron-modified activated carbon. Water Res 41(9):1851–1858. doi:10.1016/j.watres.2007.01.052

Cheraghalia R, Tavakoli H, Sepehrian H (2013) Preparation characterization and lead sorption performance of alginate-SBA-15 composite as a novel adsorbent. Scientia Iranica Trans F Nanotechnol 20:1028–1034. doi:10.1016/j.scient.2013.05.013

Cheung CW, Chan CK, Porter JF, McKay G (2001) Combined diffusion model for the sorption of cadmium copper and zinc ions onto bone char. Environ Sci Technol 35(7):1511–1522. doi:10.1021/es0012725

Cotter-Howels J, Thornton L (1991) Sources and pathways of environmental lead to children in a Derbyshire mining village. Environ Geochem Health 13(2):127–135

Couillard D (1992) Appropriate waste water management technologies using peat. J Environ Syst 21:1–19. doi:10.1007/s10098-013-0635-1

Couillard D (1994) The use of peat in wastewater treatment- a review. Water Res 28:1261–1274. doi:10.1016/0043-1354(94)90291-7

Deorkar NV, Tavlarides LL (1997) A chemically bonded adsorbent for separation of antimony copper and lead. Hydrometallurgy 46:121–135. doi:10.1016/S0304-386X (97)00006-6

Devi RR, Umlong IM, Das B, Borah K, Thakur AJ, Raul PK, Banerjee S, Singh L (2014) Removal of iron and arsenic (III) from drinking water using iron oxide-coated sand and limestone. Appl Water Sci 4:75–182. doi: 10.1007/s13201-013-0139-5

Di Natale F, Lancia A, Molino A, Di Natale M, Karatza D, Musmarra D (2006) Groundwater protection from cadmium contamination by permeable reactive barriers. J Hazard Mater 160:428–434. doi:10.1016/j.jhazmat.2008.03.015

Dias Filho N, Polito W, Gushikem Y (1995) Sorption and preconcentration of some heavy metals by 2-mercaptobenzothiazole-clay. Talanta 42:1031–1036. doi:10.1016/0039-9140(95)01505-6

Dias JM, Alvim-Ferraz MCM, Almeida MF, Rivera-Utrilla J, Sánchez-Polo M (2007) Waste materials for activated carbon preparation and its use in aqueous-phase treatment: a review. J Environ Manag 85:833–846. doi:10.1016/j.jenvman.2007.07.031

Dong J, Xu Z, Wang F (2008) Engineering and characterization of mesoporous silica-coated magnetic particles for mercury removal from industrial effluents. Appl Surf Sci 254:3522–3530. doi:10.1016/j.apsusc.2007.11.048

Dousová B, Grygar T, Martaus A, Fuitová L, Kolousek D, Machovic V (2006) Sorption of As (V) on aluminosilicates treated with Fe(II) nanoparticles. J Colloid Interf Sci 15 302 (2):424–431. doi:10.1016/j.jcis.2006.06.054

Dwivedi CP, Sahu JN, Mohanty CR, Mohana BR, Meikap BCJ (2008) Column performance of granular activated carbon packed bed for Pb(II) removal. J Hazard Mater 156:596–603. doi:10.1016/j.jhazmat.2007.12.097

Eckel H (2005) Assessment and reduction of heavy metal input into agro-ecosystems: final report of the EU-Concerted Action AROMIS. Landwirtschaftsverl, Munster

Edwards M (1994) Chemistry of arsenic removal during coagulation and Fe–Mn oxidation. J Am Water Works Assoc 86(9):64–78. doi:10.5942/jawwa.2012.104.0072

Ekinci T, Budinova F, Yardim N, Petrov M, Razvigorova V, Minkova V (2002) Removal of mercury ion from aqueous solution by activated carbons obtained from biomass and coals. Fuel Process Technol 77–78:437–443. doi:10.1016/S0378-3820(02)00065-6

Elizalde-Gonzáleza MP, Mattusch J, Einicke W-D, Wennrich R (2001) Sorption on natural solids for arsenic removal. Chem Eng J 81(1–3):187–195, https://doi.org/10.1016/S1385-8947(00)00201-1

Enders R, Jekel M (1996) Adsorption und Mitfa¨llung von Antimony(III) bei der Hydroxid-fa¨llung verschiedener Metalle. Von Wasser 86:141–155

Fenga D, Aldrich C (2004) Adsorption of heavy metals by biomaterials derived from the marine alga Ecklonia maxima. Hydrometallurgy 73:1–10. doi:10.1016/s0304-386x (03) 00138-5

Ferro-Garcia MA, Rivera-Utrilla J, Rodriguez-Gordillo J, Isidora-Bautista-Toledo M (1988) Adsorption of zinc, cadmium, copper on activated carbon obtained from agricultural by-products. Carbon 26(3):363–373. doi:10.1016/0008-6223(88)90228-X

Filella M, Belzile N, Chen YW (2002) Antimony in the environment: a review focused on natural waters II. Relevant solution chemistry. Earth Sci Rev 57:125–176. doi:10.1016/S0012-8252(01)00070-8

Fu F, Wang Q (2011) Removal of heavy metal ions from wastewaters: a review. J Environ Manag 92:407–418. doi:10.4236/oalib.preprints.1200056

Fujita T, Dodbiba G, Sadaki J, Shibayama A (2006) Removal of anionic metal ions from wastewater by hydroxide-type adsorbents. Chin J Process Eng 6(3): 357–362. Article ID: 1009−606X 03–0357−06

Gaballah D, Goy E, Allain G, Kilbertus, Thaur'ont J (1997) Recovery of copper through decontamination of synthetic solutions using modified barks. Metall Mater Trans B Process Metall Mater Process Sci 28(1): 13–23. doi: 10.1007/s11663-997-0122-3

Gebel T (1997) Arsenic and antimony: comparative approach on mechanistic toxicology. Chem Biol Interact 107(3):131–144. doi:10.1016/S0009-2797(97)00087-2

Geetha V, Singh RK, Sahu V (2013) A comparative study on the removal of heavy metals by adsorption using fly ash and sludge: a review. Int J Appl Innov Eng Manag 2(7):45–56

Ghimire KN, Inoue K, Yagamuchi H, Makino K, Mijayima T (2003) Adsorptive separation of arsenate and arsenite anions from aqueous medium by using orange waste. Water Res 37:4945–4953. doi:10.1016/j.watres.2003.08.029

Ghodbane I, Nouri L, Hamdaoui O, Chiha M (2008) Kinetic and equilibrium study for the sorption of cadmium (II) ions from aqueous phase by eucalyptus bark. J Hazard Mater 152:148–158. doi:10.1016/j.jhazmat.2007.06.079

Giraldo L, Moreno-Pirajan JC (2008) Pb^{2+} adsorption from aqueous solutions on activated carbons obtained from lignocellulosic residues. Braz J Chem Eng 25:143–151. doi:10.1590/S0104-66322008000100015

Goh GH, Lim TT (2004) Geochemistry of inorganic arsenic and selenium in a tropical soil: effect of reaction time pH and competitive anions on arsenic and selenium adsorption. Chemosphere 55:849–859. doi:10.1016/j.chemosphere.2003.11.041

Goldberg S (2002) Competitive adsorption of arsenate and arsenite on oxides and clay minerals. Soil Sci Soc Am J 66:413–421. doi:10.2136/ sssaj2002.4130

Gomez-serrano V, Macias-garcia A, Espinosa-mansilla A, Valenzuela-Calahorro C (1998) Adsorption of mercury cadmium and lead from aqueous solution on heat-treated and sulphurized activated carbon. Water Res 32(1):1–4. doi:10.1016/s0043-1354(97)00203-0

Gu Z, Deng B, Yang J (2007) Synthesis and evaluation of iron-containing ordered mesoporous carbon (FeOMC) for arsenic adsorption. Microporous Mesoporous Mater 102:265–273. doi:10.1016/j.micromeso.2007.01.011

Gueu S, Yao B, Adouby K, Ado G (2007) Kinetics and thermodynamics study of lead adsorption on to activated carbons from coconut and seed hull of the palm tree. Int J Environ Sci Technol 4:11–17. doi:10.1007/bf03325956

Gülbaş G, Tirtom VN, Çelik A, Dost K (2011) Arsenic removal from aqueous system using natural and modified (Kula ebonite and zeolite) adsorbents. Environ Prog Sustain Energy 31(3):443–448. doi:10.1002/ep.10573

Guo X, Wu Z, He M (2009) Removal of antimony(V) and antimony(III) from drinking water by coagulation-flocculation-sedimentation (CFS). Water Res 43(17):4327–4335. doi:10.1016/j.watres.2009.06.033

Guo H, Li Y, Zhao K, Ren Y, Wei C (2011) Removal of arsenite from water by synthetic siderite: behaviors and mechanisms. J Hazard Mater 186:1847–1854. doi: 10.1016/j.jhazmat.2010.12.078

Gupta VK, Rastogi A (2008) Biosorption of lead(II) from aqueous solutions by non-living algal biomass *Oedogonium* sp. and *Nostoc* sp. – a comparative study. Colloids Surf B Biointerfaces 64(2):170–178. doi:10.1016/j.colsurfb.2008.01.019

Gupta A, Yunus M, Sankararamakrishnan N (2012) Zerovalent iron encapsulated chitosan nanospheres - a novel adsorbent for the removal of total inorganic arsenic from aqueous systems. Chemosphere 86(2):150–155. doi:10.1016/j.chemosphere.2011.10.003

Gupta VK, Saini VK, Jain N (2005) Adsorption of As(III) from aqueous solutions by iron oxide-coated sand. J Colloid Interface Sci 288(1):55–60. doi:10.1016/j.jcis.2005.02.054

Gupta A, Yunus M, Sankararamakrishnan N (2012) Zerovalent iron encapsulated chitosan nanospheres - a novel adsorbent for the removal of total inorganic arsenic from aqueous systems. Chemosphere 86(2):150–155. doi:10.1016/j.chemosphere.2011.10.003

Hansen HK, Rojo A, Oyarzun C, Ottosen LM, Ribeiro A, Mateus E (2006) Biosorption of arsenic (V) with Lessonia nigrescens in wastewater from copper smelting. Miner Eng 19(5):486–490. doi:10.1016/j.mineng.2005.08.018

Herrero R, Lodeiro P, Rey-Castro C, Vilarino T, Sastre de Vicente M (2005) Removal of inorganic mercury from aqueous solution by biomass of the marine microalga *Cystoceira baccata*. Water Res 39:3199–3210. doi:10.1016/j.watres.2005.05.041

Hlavay J, Polyak K (2005) Determination of surface properties of iron-hydroxide-coated coated alumina adsorbent prepared for removal of arsenic from drinking water. J Colloid Interface Sci 284:71–77. doi:10.1016/j.jcis.2004.10.032

Hooda PS, Alloway BJ (1998) Cadmium and lead sorption behaviour of selected English and Indian soils. Geoderma 84:121–134, https://doi.org/10.1016/S0016-7061(97)00124-9

Horsfall M Jr, Abiba AA (2003) Sorption of cadmium (II) and zinc (II) ions from aqueous solutions by cassava waste biomass (*Manihot esculenta* Cranz). Water Res 37 (20):4913–4923. doi:10.1016/j.watres.2003.08.020

Horsfall M Jr, Abiba AA, Spiff AI (2003) Removal of Cu (II) and Zn (II) ions from wastewater by cassava (*Manihot esculenta* Cranz) waste biomass. Afr J Biotechnol 2(10):360–364. doi:10.5897/AJB2003.000-1074

Hossain MS, Islam MR (2008) Experimental and numerical modeling of arsenic transport in limestone. Energy Sour Part A 30:1189–1201. doi: 10.1080/15567030601100670

Hsu JC, Lin CJ, Liao CH, Chen ST (2008) Removal of As(V) and As(III) by reclaimed iron-oxide coated sands. J Hazard Mater 153(1–2):817–826, https://doi.org/10.1016/j.jhazmat.2007.09.031

Hua Z, Lv Q, Ye W, Wong CK, Cai G, Gu D (2006) MiRNA-directed regulation of VEGF and other angiogenic factors under hypoxia. PLos One 1:e-116. doi:10.1371/journal.pone.0000116

Husein DZ (2013) Adsorption and removal of mercury ions from aqueous solution using raw and chemically modified Egyptian mandarin peel. Desalin Water Treat 51(34–36):6761–6769. doi:10.1080/19443994.2013.801793

Ibrahim SC, Hanafia MAKM, Yahya MAZ (2006) Removal of cadmium from aqueous solutions by adsorption onto sugarcane bagasse. Am-Eur J Agric Environ 1(3):179–184

Igwe JC, Abia AA, Oakpareke OC (2005) Sorption kinetics and intraparticulate diffusivities of Co Fe and Cu ions on EDTA-modified maize cob. Int J Chem 15(3):187–191. doi:10.1590/s0100-46702007000100005

Ilavsky J (2008) Removal of antimony from water by sorption materials. Slovak J Civil Eng 2:1–6

Ilavský J, Barloková D, Munka K (2015) Iron-based sorption materials for the removal of antimony from water. Water Air Soil Pollut 226:2238. doi:10.1007/s11270-014-2238-9

Inglezakis VJ, Grigoropoulou HP (2003) Modeling of ion exchange of Pb^{2+} in fixed beds of clinoptilolite. Microporous Mesoporous Mater 61:273–282. doi:10.1016/S1387-1811(03)00374-3

Ismail AA, El-Midany AA, Ibrahim IA, Matsunaga H (2008) Heavy metal removal using SiO_2-TiO_2 binary oxide: experimental design approach. Adsorp J Int Adsorp Soc 14:21–29. doi:10.1007/s10450-007-9042-4

Jarup L (2003) Impact of environmental pollution on health: balancing risk. Br Med Bull 68:167–182. doi:10.1093/bmb/ldg024

Jessen S, Larsen F, Koch CB, Arvin E (2005) Sorption and desorption of arsenic to ferrihydrite in a sand filter. Environ Sci Technol 39:8045–8051. doi:10.1021/es050692x

Kadirvelu K, Sivasankaric C, Jambuligam M, Pattabhi S (2001) Activated carbon from *Parthenium* as adsorbent: adsorption of Hg(II) from aqueous solution. Indian J Chem Technol 9:499–503

Kalfa OM, Yalçinkaya O, Türker AR (2009) Synthesis of nano B_2O_3/TiO_2 composite material as a new solid phase extractor and its application to preconcentration and separation of cadmium. J Hazard Mater 166:455–461. doi:10.1016/j.jhazmat.2008.11.112

Kamala CT, Chu KH, Chary NS, Pandey PK, Ramesh SL, Sastry AR, Sekhar KC (2005) Removal of arsenic(III) from aqueous solutions using fresh and immobilized plant biomass. Water Res 39(13):2815–2826. doi:10.1016/j.watres.2005.04.059

Kamsonlian S, Suresh S, Balomajumder C, Chand S (2011) Biosorption of Cd(II)and As(III) ions from aqueous solution by tea waste biomass. Afr J Environ Sci Technol 5:1–7

Kargi F, Cikla S (2006) Zinc (II) ion recovery by biosorption onto powdered waste sludge (PWS): effects of operating conditions. J Chem Technol Biotechnol 81(0):1661–1668. doi: 10.1002/jctb.1585

Karnitz O, Gurgel LVA, de Melo JCP, Botaro VR, Melo TMS, de Freitas Gil RP, Gil LF (2006) Adsorption of heavy metal ion from aqueous single metal solution by chemically modified sugarcane bagasse. Bioresour Technol 98:1291–1297. doi:10.1016/j.biortech.2006.05.013

Karthikeyan J, Chaudhuri M (1986) Enhancement of mercury(II) sorption from water by coal through chemical pretreatment. Water Res 20:449–452. doi:10.1016/0043-1354(86)90192-2

Katsoyiannis IA, Zouboulis AI, Jekel M (2004) Kinetics of bacterial As(III) oxidation and subsequent As(V) sorption onto biogenic manganese oxides during groundwater treatment. Ind Eng Chem Res 43:486. doi:10.1021/ie030525a

Katsumata H, Kaneco S, Inomata K, Itoh K, Funasaka K, Masuyama K, Suzuki T, Ohta K (2003) Removal of heavy metals in rinsing waste water from plating factory by adsorption with economical viable materials. J Environ Manag 69(2):187–191. doi:10.1016/s0301-4797(03)00145-2

Kesenci K, Say R, Denizli A (2002) Removal of heavy metal ions from water by using poly (ethyleneglycol dimethacrylate-co-acrylamide) beads. Eur Polym J 38(7):1443–1448. doi:10.1016/s0014-3057(01)00311-1

Khalid N, Ahmad S, Toheed A, Ahmed J (2000) Potential of rice husks for antimony removal. Appl Radiat Isot 52(1):31–38. doi:10.1016/s0969-8043(99)00115-3

Kinniburgh DG, Smedley PL (2001) Arsenic contamination of ground water in Bangladesh, vol. 2 Final Report (BGS Technical report WC/00/19 British Geological Survey, Keyworth, UK

Klimko T, Lalinska B, Majzlan J, Chovan M, Kucerova G, Paul C (2011) Chemical composition of weathering products in neutral and acidic mine tailings from stibnite exploitation in Slovakia. J Geosci 56(3):327–340. doi:10.3190/jgeosci.104

Krishnaswamy K, Kumar BD (1998) Lead toxicity. Indian J Paediat 35:209–216

Kula I, Uğurlu M, Karaoğlu H, Çelik A (2008) Adsorption of Cd(II) ions from aqueous solutions using activated carbon prepared from olive stone by ZnCl activation. Bioresour Technol 99(3):492–501. doi:10.1016/j.biortech.2007.01.015

Kumar U, Bandyopadhyay M (2006) Sorption of cadmium from aqueous solution using pretreated rice husk. Bioresour Technol 97(1):104–109. doi:10.1016/j.biortech.2005.02.027

Kundu S, Pal A, Mandal M, Kumar S (2004) Hardened paste of Portland cement – a new low-cost adsorbent for the removal of arsenic from water. J Environ Sci Health A 39:185–202. doi:10.1081/ese-120027377

Lahmann E, Munari S, Amicarelli V, Abbaticchio P, Gabellieri (1986) Heavy metals: identification of air quality and environmental problems in the European Community, Vol 1 and 2. Luxembourg, Commission of the European Communities, Report No. EUR 10678 EN/I and EUR 10678 EN/II

Lakshmipathiraj P, Narasimhan BRV, Raju GB (2006) Adsorption of arsenate on synthetic goethite from aqueous solutions. J Hazard Mater 136(2):281–287, https://doi.org/10.1016/j.jhazmat.2005.12.015

Leuz K, Hug SJ, Wehrli B, Johnson CA (2006) Sorption of Sb(III) and Sb(V) to goethite: influence on Sb(III) oxidation and mobilization. Environ Sci Technol 40:7277–7282. doi:10.1021/es061284b

Leyva AG, Marrero J, Smichowski P, Cicerone D (2001) Sorption of antimony onto hydroxyapatite. Environ Sci Technol 35(18):3669–3675. doi:10.1021/es0009929

Li Z, Beachner R, Mcmanama Z, Hanlie H (2007) Sorption of arsenic by surfactant modified zeolite and kaolinite. Microporous Mesoporous Mater 05:291–297. doi:10.1016/j.micromeso.2007.03.038

Li B, Zhang Y, Ma D, Shi Z, Ma S (2014) Mercury nano-trap for effective and efficient removal of mercury(II) from aqueous solution. Nat Commun 5:5537. doi:10.1038/ncomms6537

Lijzen JPA, Ekelenkamp A (1995) Bronnen van diffuse bodembelasting [Sources of diffuse soil pollution]. Dutch Natl Inst Human Health Environ (RIVM), Bilthoven

Liu JF, Zhao ZS, Jiang GB (2008) Coating Fe_3O_4 magnetic nanoparticles with humic acid for high efficient removal of heavy metals in water. Environ Sci Technol 42:6949–6954. doi:10.1021/es800924c

Liu B, Wang D, Li H, Xu Y, Zhang L (2011) As(III) removal from aqueous solution using α-Fe_2O_3 impregnated chitosan beads with As(III) as imprinted ions. Desalination 272:286–292. doi: 10.1016/j.desal.2011.01.034

Liu M, Hou L, Xi B, Zhao Y, Xia X (2013) Synthesis, characterization, and mercury adsorption properties of hybrid mesoporous aluminosilicate sieve prepared with fly ash. Appl Surf Sci 273:706–716. doi:10.1016/j.apsusc.2013.02.116

Lone MI, He ZL, Stoffella PJ, Yang XE (2008) Phytoremediation of heavy metal polluted soils and water: progresses and perspectives. J Zhejiang Univ Sci B 9(3):210–220. doi:10.1631/jzus.b0710633

Lopez Delgado A, Perez C, Lopez FA (1998) Sorption of heavy metals on blast furnace sludge. Water Res 32:989. doi: 10.1016/s0043-1354(97)00304-7

Lorenzen L, Van Deventer JSJ, Landi WM (1995) Factor affecting the mechanism of the adsorption of arsenic species on activated carbon. Min Eng 8(45):557–569. doi:10.1016/0892-6875(95)00017-k

Luxton T, Tadanier CJ, Eick MJ (2006) Mobilization of arsenite by competitive interaction with silicic acid. Soil Sci Soc Am J 70:204–214. doi:10.2136/sssaj2005.0101

Ma QY, Logan TJ, Traina SJ (1995) Lead immobilization from aqueous solutions and contaminated soils using phosphate rocks. Environ Sci Technol 29:1118–1126. doi:10.1021/es00004a034

Macías-García A, Gómez-Serrano V, Alexandre-Franco MF, Valenzuela-Calahorro C (2003) Adsorption of cadmium by sulphur dioxide treated activated carbon. J Hazard Mater 1:103 (1–2):141–152. doi: 10.1016/s0304-3894(03)00243-7

Maiti A, Basu JK, De S (2010) Development of a treated laterite for arsenic adsorption: effects of treatment parameters. Ind Eng Chem Res 49(10):4873–4886. doi:10.1021/ie100612u

Maji SK, Pal A, Pal T (2007) Arsenic removal from aqueous solutions by adsorption on laterite soil. J Environ Sci Health Part A Toxic/Hazard Subst Environ 42:453–462. doi: 10.1080/10934520601187658

Manaka M (2006) Amount of amorphous materials in relationship to arsenic, antimony and bismuth concentrations in a brown forest soil. Geoderma 136:75–86. doi: 10.1016/j.geoderma.2006.02.002

Manjare SD, Sadique MH, Ghoshal AK (2005) Equilibrium and kinetics studies for As(III) adsorption on activated alumina and activated carbon. Environ Technol 26:1403–1410. doi: 10.1080/09593332608618609

María P, González E (2008) Chemically modified maize cobs waste with enhanced adsorption properties upon methyl orange and arsenic. Bioresour Technol 99(11):5134–5139, https://doi.org/10.1016/j.biortech.2007.09.023

Martins RJE, Pardo R, Boaventura RAR (2004) Cadmium (II) and zinc(II) adsorption by the aquatic moss Fontinalis antipyretica: effect of temperature pH and water hardness. Water Res 38(3):693–699. doi:10.1016/j.watres.2003.10.013

Masih D, Izumi Y, Seida Y (2009) Arsenic removal from dilute solutions by high surface area mesoporous iron oxyhydroxide. Water Air Soil Pollut Focus 9(3–4):203–211. doi:10.1007/s11267-009-9206-1

Mason B, Moore C (1982) Principles of geochemistry, 4th edn. Wiley, New York

Masue Y, Loeppert RH, Kramer TA (2007) Arsenate and arsenite adsorption and desorption behavior on coprecipitated aluminum: iron hydroxides. Environ Sci Technol 4(837):842. doi:10.1021/es061160z

Mata YN, Bl’azquez ML, Ballester A, Gonz’alez F, Mũnoz JA (2009) Sugar-beet pulp pectin gels as biosorbent for heavy metals: preparation and determination of biosorption and desorption characteristics. Chem Eng J 150(2–3):289–301. doi:10.1016/j.cej.2009.01.001

Mathialagan T, Viraraghavan T (2002) Adsorption of cadmium from aqueous solution by perlite. J Hazard Mater B94:291–303. doi:10.1016/s0304-3894(02)00084-5

Mcafee BJ, Gould WD, Nedeau JC, da Costa ACA (2001) Biosorption of metal ions using chitosan chitin and biomass of Rhizopus oryzae. Sep Sci Technol 36(14):3207–3222. doi:10.1081/ss-100107768

Mckay G, Bino MJ, Altamemi HR (1985) The adsorption of various pollutants from aqueous solutions onto activated carbon. Water Res 19:491–495. doi:10.1016/0043-1354(85)90041-7

McKay G, Blair HS, Findon A (1989) Equilibrium studies for the sorption of metal ions onto chitosan. Indian J Chem 28A:356

Meena AK, Kadirvelu K, Mishra GK, Rajagopal C, Nagar PN (2008) Adsorptive removal of heavy metals from aqueous solution by treated sawdust (*Acacia arabica*). J Hazard Mater 150:604–611. doi:10.1016/j.jhazmat.2007.05.030

Mellah A, Chegrouche S (1997) The removal of zinc from aqueous solutions by natural bentonite. Water Res 31(3):621–629. doi:10.1016/s0043-1354(96)00294-1

Meng X, Hua Z, Dermatas D, Wang W, Kuo HY (1998) Immobilization of mercury (II) in contaminated soil with used tire rubber. J Hazard Mate 57:231–241. doi:10.1016/s0304-3894(97)00091-5

Mercy SDE, Wolfgang HH (2006) Removal of selenium and antimony species from aqueous solutions by means of a weakly basic ion exchanger. Combined Hybrid Adsorb, pp 287–292. Doi: 10.1007/1-4020-5172-7_35

Mielke HW (1993) Lead dust contaminated USA communities comparison of Louisiana and Minnesota. Appl Geochem 8(2):257–261. doi:10.1016/s0883-2927(09)80046-2

Minamisawa M, Nakajima S, Minamisawa H, Yoshida S, Takai N (2005) Removal of copper (II) and cadmium(II) from water using roasted coffee beans. In: Lichtfouse E, Schwarzbauer J, Robert D (eds) Environmental chemistry for a sustainable world - green chemistry and pollutants in ecosystems. Springer, Berlin/Heidelberg, pp 259–265. doi:10.1007/3-540-26531-7_25

Mištová E, Telecká M, Parschová H, Jelínek L (2009) Selective sorption of Sb(III) oxoanion by composite sorbents based on cerium and zirconium hydrous oxides. Ion Exchang Lett 2:19–21

Mohan D, Singh KP (2002) Single- and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse - an agricultural waste. Water Res 36(9):2304–2318. doi:10.1016/s0043-1354(01)00447-x

Mohan D, Gupta VK, Srivastava SK, Chander S (2001) Kinetics of mercury adsorption from wastewater using activated carbon de-rived from fertilizer waste. Colloid Surface A 177:169–181. doi:10.1016/s0927-7757(00)00669-5

Mohan D, Pittman CU Jr, Bricka M, Smith F, Yancey B, Mohammad J, Steele PH, Alexandre-Franco MF, Serrano VG, Gong H (2007) Sorption of arsenic, cadmium, and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production. J Colloid Interf Science 310(1):57–73

Mohapatra M, Anand S (2007a) Studies on sorption of Cd (II) on Tata chromite mine overburden. J Hazard Mater 148(3):553–559. doi:10.1016/j.jhazmat.2007.03.008

Mohapatra M, Anand S (2007b) Cd (II) adsorption on high iron containing lateritic ore of Orissa. Indian J Environ Protect 27(6):509–515

Mohapatra M, Rout K, Anand S (2009) Preparation characterization and heavy metal ion adsorption on Mg(II) doped goethite. J Hazard Mater 171(1–3):417–423. doi:10.1016/j.jhazmat.2009.06.017

Montanher SF, Oliveira EA, Rollemberg MC (2005) Removal of metal ions from aqueous solutions by sorption onto rice bran. J Hazard Mater 117(2–3):207–211. doi:10.1016/j.jhazmat.2004.09.015

Motsi T, Rowson NA, Simmons MJH (2009) Adsorption of heavy metals from acid mine drainage by natural zeolite. Int J Miner Process 92(1–2):42–48. doi:10.1016/j.minpro.2009.02.005

Murugesan GS, Sathishkumar M, Swaminathan K (2006) Arsenic removal from groundwater by pretreated waste tea fungal biomass. Bioresour Technol 97(3):483–487. doi:10.1016/j.biortech.2005.03.008

Nadeem M, Shabbir M, Abdullah MA, Shah SS, McKay G (2009) Sorption of cadmium from aqueous solution by surfactant-modified carbon adsorbents. Chem Eng J 148(2–3):365–370. doi:10.1016/j.cej.2008.09.010

Nah IW, Hwang KY, Jeon C, Choi HB (2006) Removal of Pb ion from water by magnetically modified zeolite. Miner Eng 19(14):1452–1455. doi:10.1016/j.mineng.2005.12.006

Namasivayam C, Periasamy K (1993) Bicarbonate treated peanut hull carbon for mercury (II) removal from aqueous solution. Water Res 27:1663–1668. doi:10.1016/0043-1354(93)90130-a

Namasivayam C, Sangeetha D (2006) Recycling of agricultural solid waste coir pith: removal of anions heavy metals organics and dyes from water by adsorption onto $ZnCl_2$ activated coir pith carbon. J Hazard Mater B 135:449–452. doi:10.1016/j.jhazmat.2005.11.066

Namasivayam C, Senthilkumar S (1997) Recycling of industrial solid waste for the removal of mercury(II) by adsorption process. Chemosphere 34:357–375. doi:10.1016/s0045-6535(96)00383-9

Nasir K, Shujaat A, Aqidat T, Jamil A (1997) Immobilization of arsenic on rice husk. Adsorpt Sci Technol 6:655–666. doi:10.1524/ract.1998.83.3.157

Nemade PD, Kadam AM, Shankar HS (2009a) Adsorption of arsenic from aqueous solution on naturally available red soil. J Environ Biol 30(4):499–504

Nemade P, Kadam AM, Shankar HS (2009b) Removal of iron arsenic and coliform bacteria from water by novel constructed soil filter system. Ecol Eng 35(8):1152–1157. doi:10.1016/j.ecoleng.2009.03.013

Ngah WSW, Hanafiah (2008) Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: a review. Bioresour Technol 99:3935–3948. doi:10.1016/j.biortech.2007.06.011

Ngo HH, Vigneswaran S, Hu JY, Thirunavukkarasu O, Viraraghava T (2002) A comparison of conventional and non-conventional treatment technologies on arsenic removal from water. Water Sci Technol Water Supply 2(5–6):119–125

Nilchi A, Garmarodi SR, Darzi S (2010) Removal of arsenic from aqueous solutions by an adsorption process with Titania-Silica binary oxide nanoparticle loaded polyacrylonitrile polymer. J Appl Polym Sci 119:3495–3504. doi:10.1002/app.33003

Nishigandha JB, Suryavanshi AA, Tirthakar SN (2015) Removal of heavy metal lead (pb) from electrochemical industry waste water using low cost adsorbent. Int J Res Eng Technol 04:731–733

Norton L, Baskaran K, McKenzie T (2004) Biosorption of zinc from aqueous solutions using biosolids. Adv Environ Res 8(3–4):629–635. doi:10.1016/s1093-0191(03)00035-2

Nriagu J (2005) Keynote lecture at the 1st International Workshop on Antimony in the Environment, Heidelberg, Germany

Otero M, Rozada F, Moran A, Calvo LF, Garcia AI (2009) Removal of heavy metals from aqueous solutions by sewage sludge based sorbents: competitive effects. Desalination 239:46–57. doi:10.1016/j.desal.2008.03.005

Ouma R, Mude A, De Steeg JV (2011) Dealing with climate-related risks: some pioneering ideas for enhanced pastoral risk amnagament in Africa (Assessing and Addressing Climate-Induced Risk in Sub-Saharan Rainfed Agriculture). Experimental Agriculture 47(2):375–393

Ozdes D, Gundogdu A, Kemer B, Duran C, Senturk HB, Soylak M (2009) Removal of Pb(II) ions from aqueous solution by a waste mud from copper mine industry: equilibrium kinetic and thermodynamic study. J Hazard Mater 166:1480–1487. doi:10.1016/j.jhazmat.2008.12.073

Park HJ, Jeong SW, Yang JK, Kim BG, Lee SM (2007) Removal of heavy metals using waste eggshell. J Environ Sci 19(12):1436–1441. doi:10.1016/s1001-0742(07)60234-4

Pavasant P, Apiratikul R, Sungkhum V, Suthiparinyanont P, Wattanachira S, Marhaba TF (2006) Biosorption of Cu Cd Pb and Zn using dried marine green macroalga *Caulerpa lentillifera*. Bioresour Technol 97(18):2321–2329. doi:10.1016/j.biortech.2005.10.032

Pehlivan E, Altun T, Cetin S, Bhanger MI (2009) Lead sorption by waste biomass of hazelnut and almond shell. J Hazard Mater 167(1-3):1203–1208. doi:10.1016/j.jhazmat.2009.01.126

Peniche-Covas C, Alvarez LW, Arguelles-Monal W (1992) The adsorption of mercuric ions by chitosan. J Appl Polym Sci 46:1147–1150. doi:10.1002/app.1992.070460703

Petrilli FL, De Flora S (1978) Metabolic deactivation of hexavalent chromium mutagenicity. Mutat Res 54(2):139–147. doi:10.1016/0165-1161(78)90034-1

Pokhrel D, Viraraghavan T (2008) Arsenic removal from aqueous solution by iron oxide-coated biomass: common ion effects and thermodynamic analysis. Sep Sci Technol 43:3545–3562. doi:10.1080/01496390802212609

Polowczyk I, Bastrzyk A, Koźlecki T, Rudnicki P, Sawiński Sadowski Z, Sokołowski A. (2007) Application of fly ash agglomerates in the sorption of arsenic. Polish J Chem Technol 9 (2):37–41. doi: 10.2478/v10026-007-0022-y

Potgieter JH, Potgieter-vermaak SS, Modise J, Basson N (2005) Removal of iron and manganese from water with a high organic carbon loading. Part II: the effect of various adsorbents and nanofiltration membranes. Water Air Soil Pollut 162:61–70. doi:10.1007/s11270-005-5993-9

Pragati P, Trivedia SS, Pandey L (2015) Removal of zinc from synthetic waste water by saw dust as an adsorbent. Int J Innov Sci Eng Technol 16(2):120–127

Prased KS, Srivastava P, Subramaniyan V, Paul J (2011) Biosorption of As(III) ion on *Rhodococcus* sp. WB-12: biomass characterization and kinetic studies. Sep Sci Technol 46(16):2517–2525. doi:10.1080/01496395.2011.597040

Qui J, Zhang G, Li H (2015) Efficient removal of arsenic from water using a granular adsorbent: Fe-Mn binary oxide impregnated chitosan bead. Bioresour Technol 193:243–249. doi:10.1016/j.biortech.2015.06.102

Rahbar N, Jahangiri A, Boumi S, Khodayar MK (2014) Mercury removal from aqueous solutions with chitosan-coated magnetite nanoparticles optimized using the box-Behnken design. Jundishapur J Nat Pharm Prod 9(2):e15913

Rahman (2004) Present status of ground water arsenic contamination in Bangladesh and detailed study of Murshidabad one of the affected neighbouring districts in West Bengal. PhD thesis, Jadavpur University, India

Raji A, Anirudhan TS (1996) Removal of Hg(II) from aqueous solution by sorption on polymerized saw dust. Indian J Chem Technol 3:49–54

Ramos RL, Jacome LAB, Rodriguez IA (2005) Adsorption of cadmium(II) from aqueous solution on natural and oxidized corncob. Sep Purif Technol 4:41–49. doi:10.1016/j.seppur.2005.02.005

Rana MS, Halim MA, Waliul Hoque SAM, Hasan K, Hossain MK (2009) Bioadsorbtion of arsenic by prepared and commercial crab shell chitosan. Biotechnology 8:160–165. doi:10.3923/biotech.2009.160.165

Rangel JID, Solache-Rio M, Badillo-Almaraz VEJ (2006) Comparison of three Mexican aluminosilicates for the sorption of cadmium. Radioanalyt Nucl Chem 267(1):139–145. doi:10.1007/s10967-006-0020-1

Rangel-Mendez JR, Tai MH, Streat M (2000) Removal of cadmium using electrochemically oxidized activated carbon. Process Saf Environ Prot 78(2):143–148. doi:10.1205/095758200530529

Rao MM, Ramana DK, Seshaiah K, Wang MC, Chien SWC (2009) Removal of some metal ions by activated carbon prepared from *Phaseolus aureus* hulls. J Hazard Mater 166:1006–1013. doi:10.1016/j.jhazmat.2008.12.002

Rao KS, Anand S, Venkateswarlu P (2010) Adsorption of cadmium (II) ions from aqueous solutions by *Tectona Grandis* L.F. (Teak leaves powder). BioResources 5(1):438–454, http://ncsu.edu/bioresources. ISSN: 1930–2126

Rashed MN (2006) Fruits stones as adsorbents for the removal of lead ion from polluted water. Environ Monit Assess 119(1–3):31–41. doi:10.1007/s10661-005-9002-y

Reddad Z, Gerente C, Andres Y, LeCloirec P (2002) Adsorption of several metal ions onto a low-cost biosorbent: kinetic and equilibrium studies. Environ Sci Technol 36(9):2067–2073. doi:10.1021/es0102989

Ren ZM, Zhang GS, Chen JP (2011) Adsorptive removal of arsenic by an iron – zirconium binary oxide adsorbent from water. J Colloid Interf Sci 358:230–237. doi: 10.1016/j.jcis.2011.01.013

Ricordel S, Taha S, Cisse I, Dorange G (2001) Heavy metals removal by adsorption onto peanut husks carbon: Characterization kinetics study and modeling. Sep Purif Technol 24:389–401. doi:10.1016/s1383-5866(01)00139-3

Ridvan R, Yılmaz N, Denizli A (2003) Biosorption of cadmium lead mercury and arsenic ions by the fungus *Penicillium purpurogenum*. Separ Sci Technol 38(9):2039–2053. doi: 10.1081/ss-120020133

Robert GR Jr. (2000) U.S. Geological survey minerals yearbook-2000

Rout K, Mohapatra M, Anand S (2009) Lead, cadmium and zinc adsorption on low grade bauxite ore. Indian J Environ Prot 29(1):30–35

Saeed A, Akhter MW, Iqbal M (2005a) Removal and recovery of heavy metals from aqueous solution using papaya wood as a new biosorbent. Sep Purif Technol 45(1):25–31. doi:10.1016/j.seppur.2005.02.004

Saeed A, Iqbal M, Akhtar MW (2005b) Removal and recovery of lead (II) from single and multimetal (Cd Cu Ni Zn) solutions by crop milling waste (black gram husk). J Hazard Mater 117(1):65–73. doi:10.1016/j.jhazmat.2004.09.008

Sari A, Tuzen M (2008) Biosorption of cadmium(II) from aqueous solution by red algae (*Ceramium virgatum*): equilibrium kinetic and thermodynamic studies. J Hazard Mater 157 (2–3):448–454. doi:10.1016/j.jhazmat.2008.01.008

Sarı A, Citak D, Tuzen M (2010) Equilibrium thermodynamic and kinetic studies on adsorption of Sb(III) from aqueous solution using low-cost natural diatomite. Chem Eng J 162:521–527. doi:10.1016/j.cej.2010.05.054

Sarkar P, Pal P, Bhattacharyay D, Banerjee S (2010) Removal of arsenic from drinking water by ferric hydroxide microcapsule-loaded alginate beads in packed adsorption column. J Environ Sci Health Part A 45:1750–1757. doi:10.1080/10934529.2010.513267

Sawalha MF, Peralta-Videa JR, Romero-Gonzalez J, Duarte-Gardea M, Gardea-Torresdey JL (2007) Thermodynamic and isotherm studies of the biosorption of Cu(II) Pb(II) and Zn (II) by leaves of saltbush (*Atriplex canescens*). J Chem Thermodyn 39(3):488–492. doi:10.1016/j.jct.2006.07.020

Say R, Birlik E, Erdemgil Z, Denizli A, Ersöz A (2008) Removal of mercury species with dithiocarbamate-anchored polymer/organosmectite composites. J Hazard Mater 150:560–564. doi:10.1016/j.jhazmat.2007.03.089

Schiewer S, Patil SB (2008) Modeling the effect of pH on biosorption of heavy metals by citrus peels. J Hazard Mater 157(1):8–17. doi:10.1016/j.jhazmat.2007.12.076

Sciban M, Klasnja M, Skrbic B (2006a) Modified hardwood sawdust as adsorbent of heavy metal ions from water. Wood Sci Technol 40(3):217–227. doi:10.1007/s00226-005-0061-6

Sciban M, Klasnja M, Skrbic B (2006b) Modified softwood sawdust as adsorbent of heavy metal ions from water. J Hazard Mater 136(2):266–271. doi:10.1016/j.jhazmat.2005.12.009

Selvaraj K, Chandramohan V, Pattabhi S (1998) Removal of Hg(II) from aqueous solution and chlor-alkali industry waste water using photo film waste sludge. J Sci Ind Res 57:271–278

Sen K, Arnab KD (1987) Adsorption of mercury(II) by coal fly ash. Water Res 21:885–888. doi:10.1016/s0043-1354(87)80003-9

Seyedi SM, Anvaripour B, Motavassel M, Jadidi N (2013) Comparative Cadmium adsorption from water by nanochitosan and chitosan. International Journal of Engineering and Innovative Technology 2(9):145–148

Shahidi A, Jalilnejad N, Jalilnejad M (2015) A study on adsorption of cadmium(II) ions from aqueous solution using *Luffa cylindrical*. Desalin Water Treat 53(13):3570–3579. doi:10.1080/19443994.2013.873878

Shan C, Ma Z, Tong M (2014) Efficient removal of trace antimony(III) through adsorption by hematite modified magnetic nanoparticles. J Hazard Mater 15(268):229–236. doi:10.1016/j.jhazmat.2014.01.020

Shao W, Li D, Tomljenovic L (2008) Are there negative CNS impacts of aluminum adjuvants used in vaccines and immunotherapy? Hydrometallurgy 91:138–144

Shibi IC, Anirudhan TS (2002) Synthesis, characterization and application as a mercury (II) sorbent of banana stalk (*Musa paradisiaca*): polyacrylamide grafted copolymer bearing carboxyl groups. Ind Eng Chem Res 41:5341–5352. doi:10.1021/ie020245f

Singh AP, Srivastava KK, Shekhar H (2007) Kinetic characterization of removal of As (III) by mixed adsorbents. J Sci Ind Res 66:952–956

Smichowski P (2008) Antimony in the environment as a global pollutant: a review on analytical methodologies for its determination in aerosols. Talanta 75:2–14. doi:10.1016/j.talanta.2007.11.005

Sneddon R, Garelick H, Valsami-Jones E (2005) An investigation into arsenic(V) removal from aqueous solutions by hydroxylapatite and bone-char. Mineral Magaz 695:769–780. doi:10.1180/0026461056950287

Sölenera M, Tunalib S, Özcan AS, Özcanc A, Gedikbey T (2008) Adsorption characteristics of lead(II) ions onto the clay/poly(methoxyethyl)acrylamide (PMEA) composite from aqueous solutions. Desalination 223:308–322. doi:10.1016/j.desal.2007.01.221

Son BC, Park K, Song SH, Yoo YJ (2004) Selective biosorption of mixed heavy metal ions using polysaccharides. Korean J Chem Eng 21:1168–1172. doi:10.1007/bf02719489

Southworth G (1996) “Outfall 51 treatment system” pp. 2–2 and 2–3 in Mercury abatement report on the U. S. Department of Energy’s Oak Ridge Y-12 Plant for the Fiscal Year 1996 Y/ER-277 Oak Ridge Y-12 Plant Oak Ridge, Tennessee, USA

Southworth G (1997) Proposed experiment for SnCl treatment of outfall 200 for the purpose of Mercury removal from East Fork Poplar creek Y-12 plant oak ridge tennessee 7 pp Y/TS-1663 Martin Marietta energy systems Y-12 plant, Oak Ridge, Tennessee, USA. Doi: https://doi.org/10.2172/671899

Srivastava SK, Tyagi R, Pant N (1989) Adsorption of heavy metal ions on carbonaceous material developed from the waste slurry generated in local fertilizer plants. Water Res 23:1161–1165. doi:10.1016/0043-1354(89)90160-7

Srivastava SK, Singh AK, Sharma A (1994) Studies on the uptake of lead and zinc by lignin obtained from black liquor - a paper industry waste material. Environ Technol 15(4):353–361. doi:10.1080/09593339409385438

Stollenwerk KG (1994) Geochemical interactions between constituents in acidic ground water and alluvium in an aquifer near Globe Arizona. Appl Geochem 9(4):353–369. doi:10.1016/0883-2927(94)90058-2

Su J, Huai-Guo H, Xiao-Ying J, Lu X-Q, Zu-Liang C (2011) Synthesis characterization and kinetic of a surfactant-modified bentonite used to remove As(III) and As(V) from aqueous solution. J Hazard Mater 185:63–70. doi:10.1016/j.jhazmat.2010.08.122

Sud D, Mahajan G, Kaur MP (2008) Kinetics and equilibrium studies of Cr(VI) metal ion remediation by *Arachis hypogea* shells: a green approach. Bioresour Technol 99:6017–6027. doi:10.1016/j.biortech.2007.11.064

Sun YC, Yang JY (1999) Simultaneous determination of arsenic(III V) selenium(IV VI) and antimony(III V) in natural water by coprecipitation and neutron activation analysis. Anal Chim Acta 395:293–300. doi:10.1016/s0003-2670(99)00321-9

Suponik T, Winiarski A, Szade J (2015) Processes of removing zinc from water using zero-valent iron. Water Air Soil Pollut 226:360. doi:10.1007/s11270-015-2617-x

Tabacki M, Yilmaz M (2008) Synthesis of a chitosan linked calix[4]arene containing polysiloxane resin for removal of heavy metals and dichromate anions. Bioresour Technol 99:6642–6645. doi:10.1016/j.biortech.2007.11.066

Takahashi T, Shozugava K, Matsuo M (2010) Contribution of amorphous iron compounds to adsorptions of pentavalent antimony by soils. Water Air Soil Pollut 208:165–172. doi: 10.1007/s11270-009-0156-z

Tang W, Li Q, Shian G, Jian Shang K (2011) Arsenic (III V) removal from aqueous solution by ultrafine α-Fe_2O_3 nanoparticles synthesized from solvent thermal method. J Hazard Mater 192:131–138. doi: 10.1016/j.jhazmat.2011.04.111

Tarley CRT, Arruda MAZ (2003) Adsorbents natural and potential applications of natural sponge (Luffa cylindrica) the removal of lead in wastewater laboratory. Revista Analitica 4:26–31

Teemu H, Seppo S, Jussi M, Raija T, Kalle L (2008) Reversible surface binding of cadmium and lead by lactic acid and bifidobacteria. Int J Food Microbiol 125:170–175. doi:10.1016/j.ijfoodmicro.2008.03.041

Teixeira MC, Ciminelli VST (2005) Development of a biosorbent for arsenite: structural modeling based on X-ray spectroscopy. Environ Sci Technol 39:895–900. doi:10.1021/es049513m

Thanabalasingam P, Pickering WF (1990) Specific sorption of antimony (III) by the hydrous oxides of Mn Fe and Al. Water Air Soil Pollut 49:175–185. doi:10.1007/bf00279519

Tien VN, Chaudhary DS, Ngo HH, Vigneswaran S (2004) Arsenic in water: concerns and treatment technologies. J Ind Eng Chem 10(3):337–348

Tong S (1998) Lead exposure and cognitive development: persistence and a dynamic pattern. J Pediat Child Health 34(2):114–118. doi:10.1046/j.1440-1754.1998.00187.x

Tong S, Von Schirnding YE, Prapamontol T (2000) Environmental lead exposure: a public health problem of global dimensions. Bull World Health Org 78(9):1068–1077, http://www.who.int/bulletin/archives/78(9)1068.pdf

Tunali S, Akar T (2006) Zn(II) biosorption properties of Botrytis cinerea biomass. J Hazard Mater 131(1–3):137–145. doi:10.1016/j.jhazmat.2005.09.024

Ungureanu G, Santos S, Boaventura R, Botelho C (2015) Biosorption of antimony by brown algae *S. muticum* and *A. nodosum*. Environ Eng Manag J 14(2):455–463. doi: omicron.ch.tuiasi.ro/EEMJ/

United Nations Conference on Environment & Development Rio de Janerio Brazil 3 to 14 June 1992 – Agenda 21. Doi:10.1017/s0376892900031647

United Nations World Water Development Report (WWDR1) (2003) Water for People Water for Life, 1st edn, Japan, 22 March 2003

Vahter M (2008) Health effects of early life exposure to arsenic. Basic Clin Pharmacol Toxicol 102(2):204–211

Valko M Rhodes CJ, Moncol J, Izakovic M, Mazur M (2006) Free radicals metals and antioxidants in oxidative stress-induced cancer. Chem Biol Interact 160(1):1–40. doi: 10.1016/j.cbi.2005.12.009

Vassileva E, Varimezova B, Hadjiivanov K (1996) Column solid-phase extraction of heavy metal ions on a high surface area CeO_2 as a preconcentration method for trace determination. Anal Chim Acta 336:141–150. doi:10.1016/s0003-2670(96)00336-4

Viraragharan T, Ayyaswami A (1987) Use of peat in water pollution control: a review. Can J Civ Eng 14:230–233. doi:10.1139/l87-035

Von Bromssen M, Jakariya M, Bhattacharya P, Ahmed KM, Hasan MA (2007) Targeting low-arsenic aquifers in Matlab Upazila southeastern Bangladesh. Sci Total Environ 379(2):121–132. doi:10.1016/j.scitotenv.2006.06.028

Wan L, Li D, Zhang D, Liu X, Fu WJ, Zhu L, Deng M, Sun F, Qian M (2008) Conservation and implications of eukaryote transcriptional regulatory regions across multiple species. BMC Genomics 9:623. doi:10.1186/1471-2164-9-623

Wang EN, Karnik R (2012) Water desalination: graphene cleans up water. Nat Nanotechnol 7:552–554. doi:10.1038/nnano.2012.153

Wang S, Gao B, Zimmerman AR, Li Y, Ma L, Harris WG, Migliaccio KW (2015) Removal of arsenic by magnetic biochar prepared from pinewood and natural hematite. Bioresour Technol 175:391–395. doi:10.1016/j.biortech.2014.10.104

Wasay SA, Haron MJ, Uchiumi A, Tokunaga S (1996) Removal of arsenite and arsenate ions from aqueous solution by basic yttrium carbonate. Water Res 30(5):1143–1148. doi:10.1016/0043-1354(95)00293-6

Wasiuddin NM, Tango M, Islam MR (2002) A novel method for arsenic removal at low concentrations. Energy Sources:2031–1041. doi:10.1080/00908310290086914

Watkins R, Weiss D, Dubbin W, Peel K, Coles B, Arnold T (2006) Investigations into the kinetics and thermodynamics of Sb(III) adsorption on goethite (alpha-FeOOH). J Colloid Interface Sci 303:639–646. doi:10.1016/j.jcis.2006.08.044

Wehrli B, Stumm W (1988) Oxygenation of vanadyl (IV); effect of coordinated surface-hydroxyl groups and OH^-. Langmuir 4:753–758. doi:10.1021/la00081a045

Weng YH, Hsieh LHC, Lee HH, Li KC, Huang CP (2005) Removal of arsenic and humic substances (HSs) by electro-ultrafiltration (EUF). J Hazard Mater 122:171–176. doi:10.1016/j.jhazmat.2005.04.001

White BR, Stackhouse BT, Holcombe JA (2009) Magnetic gamma-Fe(2)O(3) nanoparticles coated with poly-l-cysteine for chelation of As(III) Cu(II) Cd(II) Ni(II) Pb(II) and Zn(II). J Hazard Mater 161:848–853. doi:10.1016/j.jhazmat.2008.04.105

Wilcke W, Döhler H (1995) Schwermetalle in der Landwirtschaft. Arbeitspapier 217, Kuratorium für Technik und Bauwesen in der Landwirtschaft, 98

WHO (1992) A Guide to the Development of on-Site Sanitation, © WHO Typeset in India Printed in England 91/8829 – Macmillan/Clays

WHO (2013) Water quality and health strategy. Geneva. http://www.who.int/water_sanitation_health/dwq/water_quality_strategy.pdf

Xi J, He M, Lin C (2010) Adsorption of antimony (V) on kaolinite as a function of pH ionic strength and humic acid. Environ Earth Sci 60:715–722. doi:10.1007/s12665-009-0209-z

Xi J, He M, Lin C (2011) Adsorption of antimony(III) and antimony(V) on bentonite: kinetics thermodynamics and anion competition. Microchem J 97:85–91. doi:10.1016/j.microc.2010.05.017

Xu Y, Nakajima T, Ohki A (2002) Adsorption and removal of arsenic(V) from drinking water by aluminum-loaded Shirasu-zeolite. J Hazard Mater 92(3):275–287. doi:10.1016/s0304-3894(02)00020-1

Yardim MF, Budinova T, Ekinci E, Petrov N, Razvigorova M, Minkova V (2003) Removal of mercury (II) from aqueous solution by activated carbon obtained from furfural. Chemosphere 52:835–841. doi:10.1016/s0045-6535(03)00267-4

Yarkandi NH (2014) Removal of lead (II) from waste water by adsorption. Int J Curr Microbiol App Sci 3(4):207–228

Yavuz CT, Mayo JT, Suchecki C, Wang JE, llsworth AZ, D'Couto H, Quevedo EP, Prakash A, Gonzalez L, Nguyen C, Kelty C, Colvin VL (2000) Pollution magnet: nano-magnetite for arsenic removal from drinking water. Environ Geochem Health 32:327–334. doi:10.1007/s10653-010-9293-y

Yu T, Wang X, Vahter M, Li Cong (2014) Removal of antimony by FeCl3-modified granular-activated carbon in aqueous solution. J Environ Eng 140(9): doi: 10.1061/(ASCE)EE.1943-7870.0000736

Zacaria R, Gerente C, Andres Y, Cloirec PL (2002) Adsorption of several metal ions onto low-cost biosorbent: kinetic and equilibrium studies. Environ Sci Technol 36:2067–2073. doi:10.1021/es0102989

Zhang FS, Itoh H (2005) Iron oxide-loaded slag for arsenic removal from aqueous system. Chemosphere 60(3):319–325. doi:10.1016/j.chemosphere.2004.12.019

Zhang QR, Pan BC, Pan BJ, Zhang WM, Jia K, Zhang QX (2008) Selective sorption of lead cadmium and zinc ions by a polymeric cation exchanger containing nano-Zr(HPO S). Environ Sci Technol 42(11):4140–4145. doi:10.1021/es800354b

Zhang S, Xu F, Wang Y, Zhang W, Peng X, Pepe F (2013) Silica modified calcium alginate-xanthan gum hybrid bead composites for the removal and recovery of Pb(II) from aqueous solution. Chem Eng J 243:33–42. doi:10.1016/j.cej.2013.08.102

Zhanga G, Qua J, Liua H, Liua R, Wu R (2007) Preparation and evaluation of a novel Fe–Mn binary oxide adsorbent for effective arsenite removal. Water Res 41(9):1921–1928

Zhao ZL, Wang XQ, Zhao C, Zhu XG, SY D (2010) Adsorption and desorption of antimony acetate on sodium montmorillonite. J Colloid Interface Sci 345:154–159. doi:10.1016/j.jcis.2010.01.054

Zhou Z, Dai C, Zhou X, Zhao J, Zhang Y (2015) The removal of antimony by novel NZVI-zeolite: the role of iron transformation. Water Air Soil Pollut 226:76. doi:10.1007/s11270-014-2293-2

Zwain HM, Dahlan I (2012) Characterization of RHA /PFA/CFA adsorbent and its equilibrium and kinetic studies for Zn^{2+} removal. Casp J Appl Sci Res 1(13):23–34

Zwain HM, Mohammadtaghi V, Irvan D (2014) Waste material adsorbents for zinc removal from wastewater: a comprehensive review. Int J Chem Engg 2014:1–13. doi:10.1155/2014/347912

Chapter 3
Metal Recovery from Industrial and Mining Wastewaters

Denys Kristalia Villa Gómez and Piet N.L. Lens

Abstract Biological sulphate-reduction is a microbial-mediated process where sulphate is reduced to sulphide, which can be used to recover metals as sulphidic precipitates. To date, this technology has been assessed at full scale to recover valuable metals such as Cu, Ni and Zn. Despite this, research gaps are still encountered in this technology for improving and expanding its scope. Accordingly, the present review discusses: (1) the state of the art of the sulphate-reduction process, (2) the substrate options available that can meet the needs of the process, (3) the bioreactor configurations and their suitability for metal recovery, (4) the principles and factors affecting metal sulphide-precipitation and (5) the basis and advances on modelling and control of the process. The high diversity and versatility of sulphate-reducing bacteria allows exploring the use of substrates and operational conditions that facilitate the recovery of metals in bioreactors. Due to the lack of organics on industrial and mining waste streams that can sustain sulphate-reducing bacteria, the selection of a degradable, cost-effective, available, and non-pollutant substrate becomes crucial for the process. Different bioreactor configurations have been tested for the removal of metals from waste streams upon variations of the several operational conditions, concentration and type of metals tested, but metal recovery is hardly reported. Sulphate-reduction modelling has been developed to predict sulphide-inhibition/toxicity, microbial competition, kinetic parameters, biofilm and granulation development, sulphide-equilibrium and for scale-up design. Physicochemical reactions such as sorption/desorption and precipitation/solubilisation are not included in sulphate-reduction models despite that they are highly important for metal recovery in these systems. Sulphide and pH control in sulphate-reducing bioreactors is inherently essential to achieve metal recovery and to avoid unnecessary electron donor addition and over production of sulphide.

D.K.V. Gómez (✉)
School of Civil Engineering, University of Queensland, St Lucia, QLD 4067, Australia
e-mail: denyskristalia@hotmail.com

P.N.L. Lens
UNESCO-IHE Institute for Water Education, Delft, The Netherlands

Department of Chemistry and Bioengineering, Tampere University of Technology, PO Box 10541, Tampere, Finland
e-mail: p.lens@un-ihe.org

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Contents

Abbreviations

COD	Chemical oxygen demand
CSTR	Completely stirred tank reactor
UAPBR	Up-flow anaerobic packed-bed reactor
GLR	Gas-lift reactor
UASB	Up-flow anaerobic sludge blanket
UFBR	Up-flow fluidized bed reactor
DFBR	Down-flow fluidized bed reactor
ABR	Anaerobic baffled reactor
MBR	Membrane (side-stream membrane or immerse) bioreactor

3.1 Introduction

Global population growth, including urbanisation and industrial prosperity, has led to a strong increase in commodities coming from mining and metal industries. Additionally, mining activities have caused pollution problems all over the world

(Pokhrel and Dubey 2013; Haslehner Roland and Stelter Benjamin 2015). Acid-mine drainage is infamous as one of the most widespread causes of pollution in the world. Acid-mine drainage is formed when pyrite and other sulphide minerals are oxidised by bacteria to produce a leachate containing dissolved metals, sulphate and acidity (Pokhrel and Dubey 2013). These issues have triggered the development of sustainable technologies to obtain metals from wastes produced from existing and past mining operations.

Metal precipitation with biogenic sulphide can be considered a sustainable technology for treating acid-mine drainage for two main reasons: (1) it allows the recovery and reuse of metals, as many metal-refining operations process sulphidic ores (Brooks 1991), and (2) biogenic sulphide, produced by sulphate-reducing bacteria, may be produced from the sulphate already present in the wastewaters coming from metal refineries and acid-mine drainage (Boonstra et al. 1999). This technology has been already assessed at full scale to recover valuable metals such as Cu, Ni and Zn from wastewaters coming from metal associated processes (Paques 2016). Despite this, the sulphate-reduction process for recovering metals presents significant challenges with respect to cost effective and reclaimable substrates, metal recovery and bioreactor configurations that facilitate the recovery of metals as well as process control and automation.

3.2 The Sulphate-Reduction Process

3.2.1 Microbial Sulphate-Reduction

Sulphate-reducing bacteria are anaerobic micro-organisms found in a wide range of different environmental conditions that are capable of reducing sulphate by using as electron donor and carbon source, hydrogen and CO_2/CO (autotrophs) or organic compounds (heterotrophs) (Parshina et al. 2010; Hao et al. 2014). The outcome of this metabolism is hydrogen sulphide and bicarbonate ions in the case of complete oxidation, and acetate when incomplete oxidation occurs (Hao et al. 2014).

Figure 3.1 shows the anaerobic degradation process and some examples of the complete oxidation of the substrates formed in each stage by sulphate-reduction. The biological reactions shown are those that have been more commonly reported in the literature. Although there are some other reports of fermentative and sulphidogenic growth on complex organic material, sugars and amino-acids (Muyzer and Stams 2008), these reaction pathways are not directly dissimilatory sulphate-reduction (Neculita et al. 2007) nor assessed in bioreactors. The syntrophic relationship between anaerobic micro-organisms promotes competition for substrates, i.e. methanogens can compete for hydrogen and acetate with sulphate-reducing bacteria, as both use these substrates as electron donor (Muyzer and Stams 2008). In recent years, sulphate-reduction with CH_4 as electron donor has been studied in bioreactors (Meulepas et al. 2010). However, the extremely low biomass growth rates (doubling time between 1.1 and 7.5 months) is limiting for biotechnological

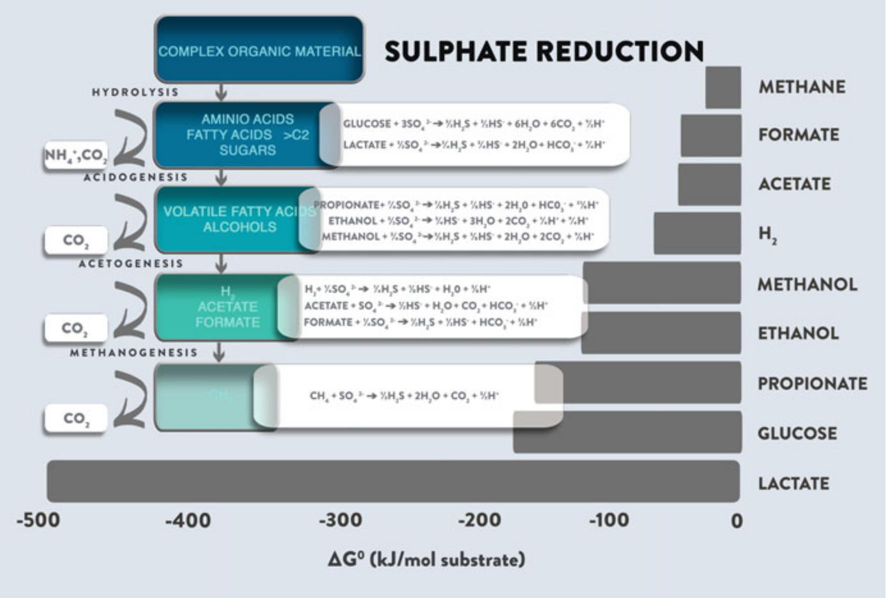


Fig. 3.1 Anaerobic degradation process of complex organic material (*left*), examples of the sulphate-reduction reactions generated from the substrates formed in each stage (*middle*) and the free Gibbs energy of the sulphate-reduction reactions with each substrate at standard conditions and pH 7 (ΔG^0) (*left*). Reactions and ΔG^0 calculated from Rittmann and McCarty (2001), half reactions for sulphate as electron acceptor and the substrates mentioned as electron donor under complete oxidation

application (Meulepas et al. 2010). The ΔG^0 values represent the amount of energy obtained from the reaction of sulphate (electron acceptor) with each substrate (electron donor) mentioned (Rittmann and McCarty 2001). Figure 3.1 shows that there is a trend in the ΔG^0 values that correlates with the location of the substrate in the anaerobic degradation stage. This explains the faster growth of sulphate-reducing bacteria on lactate ($\Delta G^0 = -492$ kJ/mol) over CH_4 ($\Delta G^0 = -21.4$ kJ/mol) as electron donor, as microorganisms obtain more energy from this reaction.

3.2.2 *Sulphate-Reducing Bacteria Diversity*

The study of sulphate-reducing bacteria diversity has been facilitated due to the increase in molecular tools available such as the use of marker genes like the 16S ribosomal RNA (rRNA) (Vanwonterghem et al. 2014; Cabezas et al. 2015). Based on this tool, sulphate-reducing bacteria can be grouped into seven phylogenetic lineages, five within the bacteria (*Deltaproteobacteria, Nitrospirae, Clostridia, Thermodesulfobacteria and Thermodesulfobiaceae*) and two within the archaea (*Euryarchaeota, and Crenarchaeota*) (Muyzer and Stams 2008).

In bioreactor systems, the diversity of sulphate-reducing bacteria highly depends on the operational conditions such as hydraulic retention time, sludge retention time, temperature, pH and salinity (Hao et al. 2014; Ňancucheo and Johnson 2012). Higher diversity is encountered in bioreactors fed with easily biodegradable compounds (Sánchez-Andrea et al. 2014; Hiibel et al. 2011) at higher COD/sulphate ratios (Deng et al. 2016) and low sulphide concentrations (Dar et al. 2009). The 16S rRNA sequences of sulphate-reducing bioreactors operating at COD/sulphate ratios of 0.2, 1 and 2 with municipal wastewater as electron donor for the treatment of acid-mine drainage, showed that the most diverse and evenly distributed microbial community was found at a COD/sulphate ratio of 2, where clones were closely related to dehalogenating and fermentative *Clostridium sp*., anaerobic sugar fermenting psychrotolerant nitrate-reducing *P. bellariivorans*, dechlorinating associated *Sedimentibacter sp*., and neutrophilic and acidophilic *Desulfovibrio sp*. and *Desulfomicrobium spp.* (Deng et al. 2016). Interestingly, literature on sulphate-reducing bioreactors operated at low pH, mimicking the pH conditions of mining waste streams (Johnson and Hallberg 2005), do not present an important decrease in sulphate-reducing bacteria diversity (Koschorreck et al. 2010; Sánchez-Andrea et al. 2014; Ňancucheo and Johnson 2012), but in the predominant species, which are *Desulfosporosinus* and *Desulfitobacterium* regardless the inoculum source (Sánchez-Andrea et al. 2014).

3.2.3 Substrates Used in Sulphate-Reduction as Electron Donor and Carbon Source

Industrial and mining waste streams usually contain low concentrations of electron donor and carbon source that can sustain sulphate-reducing activity, therefore, the selection of these, becomes of great importance. Several aspects must be considered in choosing an electron donor, including: (1) the degradation feasibility of the organic compound and biomass yield, (2) the cost of the electron donor per unit of sulphide produced, (3) the local availability of the electron donor and (4) the production of by-products that can cause pollution or toxicity problems (Dijkman et al. 1999; Kaksonen and Puhakka 2007; Liamleam and Annachhatre 2007; Papirio et al. 2012; Bijmans et al. 2011).

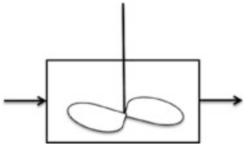
In the last years, a considerable amount of electron donors have been used in sulphate-reducing bioreactors. These can be grouped in: (a) easily biodegradable, (b) complex and (c) gaseous substrates. Easily biodegradable compounds have been largely studied and include: volatile fatty acids (acetate, propionate, pyruvate, butyrate), lactate, alcohols (methanol, ethanol), and sugars (molasses, glucose and sucrose) (Papirio et al. 2012; Liamleam and Annachhatre 2007; Kaksonen and Puhakka 2007). Most commonly, easily biodegradable compounds present more advantages over complex substrates in terms of degradation feasibility and biomass yield. Nevertheless, in many cases easily biodegradable compounds present important drawbacks regarding costs and competition with methanogens.

Complex substrates such as organic waste materials from pruning (grass clippings, leaf compost, maple wood chips and sawdust) and agriculture (straw and hay, oak chips and spent mushroom) and from cattle (manure, whey and slurry) have been studied in sulphate-reducing bioreactors for the treatment of acid-mine drainage, either as raw, composted or after silage (Lefticariu et al. 2015; Chang et al. 2000; Gibert et al. 2004; Wakeman et al. 2010; Song et al. 2012). In some cases, solid substrates from pruning and agriculture not only participate as slow releasing electron donor but also as packing material, functioning as bacterial support in bioreactors. These substrates can also retain metals via sorption mechanisms thus contributing to metal removal from the waste streams (Lefticariu et al. 2015; Neculita et al. 2007). An important drawback of these substrates is their lignocellulosic structure that prevents access to the electron donors (Wakeman et al. 2010) and the potential inhibition of the system due to volatile fatty acid accumulation (Wakeman et al. 2010; Lakaniemi et al. 2010).

Complex substrates also come from waste streams of the food, beverage and paper industry, as well as municipal wastewater (Mes et al. 2003; Deng et al. 2016; Deng and Lin 2013; Sanchez-Andrea et al. 2012; Costa et al. 2009). The most important advantages of these substrates are that they are, in many cases, cost effective (Liamleam and Annachhatre 2007), locally available (reducing transportation costs), and part of an alkaline waste stream, thus raising the pH of the metal-containing waste streams upon mixing (Deng et al. 2016). However, these substrates may not be easily biodegradable and may contain some inert material, which need to be removed by pre or post treatment (Meulepas et al. 2010; Bijmans et al. 2010; Neculita et al. 2007).

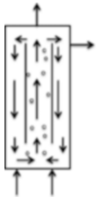
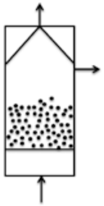
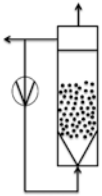
Gaseous substrates have the advantage of leaving no residual electron donor in the effluent, but they are voluminous and therefore need to be compressed during transportation (Meulepas et al. 2010). Gaseous substrates are preferable when the bioreactor operating pH is suboptimal for sulphate-reducing bacteria, as these substrates do not form toxic species upon pH variations as compared with organic substrates (Bijmans et al. 2010; Bijmans et al. 2008). Gaseous substrates used as electron donors to sustain sulphate-reduction include H_2 (coupled with CO_2 or CO as carbon source) (Parshina et al. 2010), synthesis gas ($H_2 + CO_2 + CO$) (Muyzer and Stams 2008), CO (Parshina et al. 2010) and CH_4 (Meulepas et al. 2010). Co-utilization of H_2 with CO_2 gives high sulphate-reduction rates (up to 30 g/L·d) at both mesophilic and thermophilic conditions and at laboratory and full scale (Meulepas et al. 2010; Muyzer and Stams 2008; Hao et al. 2014). The use of H_2/CO for sulphate-reduction has attracted much interest despite the low sulphate-reduction rates (up to 1.9 g/L·d) (Hao et al. 2014). This is because it may allow using cheap CO-rich synthesis gas for sulphate-reduction (Sipma et al. 2006, 2007), without the need for prior elimination of CO to prevent sulphate-reducing bacteria toxicity (Parshina et al. 2010). Progress has been made on this purpose with the recent discovery of CO tolerant sulphate-reducing bacteria species *(Desulfotomaculum kuznetsovii and Desulfotomaculum thermobenzoicum subsp.*

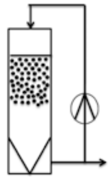
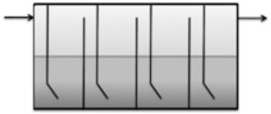
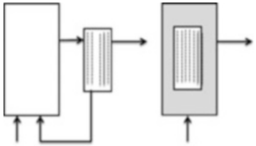
Table 3.1 Bioreactor configurations, operational conditions and results obtained in several sulphate-reducing bioreactors used for the treatment of metal containing-waste streams

Bioreactor	Configuration	Substrate	HRT (h)	T (°C)	Influent pH	COD/ SO_4^{2-} ratio	COD (g/L)	COD removal (%)	SO_4^{2-} (g/L)	SO_4^{2-} removal (%)	SO_4^{2-} removal rates (g/L·d)	Metals tested	Reference
Completely stirred tank reactor (CSTR)		Sucrose, ethanol, methanol	12–240	20–35	4.3–7.2	0.67	1.27–6.9	70–95	2.5–10	72–73	0.42–0.68	Ni, Zn, Mg, Cu	Sahinkaya et al. (2009), Greben and Maree (2005)
Up-flow anaerobic packed bed reactor (UAPBR)		Mushroom compost, compost[a], cow manure, cheese whey, wood chips, sawdust, cow manure, rice straw, wine wastes	3–480	20–25	2.6–7	1–2	3.73–5	55.4	1.5–8.5	61.8–99	0.06–0.47	Cu, Zn, Ni, As, Fe, Mg, Al, Mn, Cd, Cr	Hammack and Edenborn (1992), Jong and Parry (2003), Chang et al. 2000, La et al. (2003), Borja et al. (2010), Song et al. (2012), Costa et al. (2009)

(continued)

Table 3.1 (continued)

Bioreactor	Configuration	Substrate	HRT (h)	T (°C)	Influent pH	COD/ SO_4^{2-} ratio	COD (g/L)	COD removal (%)	SO_4^{2-} (g/L)	SO_4^{2-} removal (%)	SO_4^{2-} removal rates (g/L·d)	Metals tested	Reference
Gas lift reactor (GLR)		Synthetic gas (H_2/CO_2), H_2	24–189	20–30	2.5–5	–	–	–	0.7–30	90–99	1	Cu, Fe, Zn, Cd, Mn, Al, Mg, Ni	Muyzer and Stams (2008), Bijmans et al. (2009a), Bijmans et al. (2009b), Dijkman et al. (1999)
Up-flow anaerobic sludge bed (UASB) reactor		Lactate, ethanol, domestic wastewater-acetate	16–48	30–35	3–6.4	0.66–1.28	0.9–1	85.8–95	0.5–2.25	75–90	0.34–2	Zn, Fe, Cu	Sanchez-Andrea et al. (2012), Kaksonen et al. (2003), Sierra-Alvarez et al. (2006)
Up-flow fluidized bed reactor (UFBR)		Lactate, ethanol, domestic wastewater-acetate, *Phalaris arundinacea* plant material hydrolyzate	6.5–24	35	2.5–7.8	0.66–1	2.5–2.9	95	1.5–3.34	86	3.3–4.6	Al, Co, Cu, Fe, Ni, Pb, Zn, Mn	Lakaniemi et al. (2010), Sahinkaya et al. (2011), Sahinkaya and Gungor (2010), Kaksonen et al. (2004), Kaksonen et al. (2003)

Down-flow fluidized bed reactor (DFBR)		Ethanol, lactate	4.5–48	18–35	2–7	0.66–5	1–5	50–95mjn	1.2–3	41–88	0.9–2.6	Fe, Zn, Cd,Cu, Pb,	Sahinkaya and Gungor (2010), Gallegos-Garcia et al. (2009), Villa Gómez et al. (2015), Villa-Gómez et al. (2011)
Anaerobic bafled reactor (ABR)		Ethanol	24–48	32	3	0.67–0.74	1.2	98	3.5	90	1.2	Fe, Cu, Co, Mn, Zn, Ni	Sahinkaya and Yucesoy (2010)
Membrane bioreactor (MBR)		H_2 (50%)/ CO_2 (50%)		25–40	8.35	–	–	–	5.4	99	–	Cu, Fe, Zn, Al, Mg, Cd, Ni, Co	Tabak and Govind (2003)

Thermosyntrophicum and Desulfotomaculum carboxydivorans sp. nov.), which use CO in the presence of H_2 (Parshina et al. 2005a) or exclusively CO (Parshina et al. 2005b). This may not only allow a direct application of CO-rich synthesis gas, but also the use of CO, as sole electron donor (Sipma et al. 2006; Parshina et al. 2010).

CH_4 as electron donor for sulphate-reduction has been studied in natural environments and in bioreactors (Meulepas et al. 2010; Caldwell et al. 2008; Zhang et al. 2010). CH_4 as electron donor presents the following advantages: (a) it opens the possibility of using natural gas in sulphate-reducing bioreactors, which is less expensive and more accessible in certain world regions over other gaseous substrates, (b) the solubility of CH_4 is slightly higher compared with that of H_2 and (c) a higher number of electrons are donated per mole of compound compared to H_2 (Meulepas et al. 2010). Still, bottlenecks such as the sub-optimal conditions such as low temperatures (5–25 °C), pH above 7.5 and high salinity (30%) required to carry out the process hamper its biotechnological application.

3.2.4 Sulphate-Reducing Bioreactors and Process Configurations

Over the last years, different bioreactors have been studied for sulphate-reduction and treatment of metal containing waste streams in a single stage or in multistage process (Table 3.1). These bioreactors include: a) completely stirred tank reactor (CSTR), b) up-flow anaerobic packed-bed reactor (UAPBR), c) gas-lift reactor (GLR), d) up-flow anaerobic sludge blanket (UASB) reactor, e) up-flow fluidized bed reactor (UFBR), f) down-flow fluidized bed reactor (DFBR), g) anaerobic baffled reactor (ABR), h) membrane (side-stream membrane or immerse) bioreactor (MBR) (Kaksonen and Puhakka 2007; Papirio et al. 2012). The classifications of these systems can be based on: (a) the flow mode (batch, continuous or semi continuous), (b) biomass retention (suspended or attached), (c) state of the substrate used (liquid, gas or solid) and (d) whether is possible or not to recover the metals in a single stage, or if it requires additional stages (multistage process).

A single stage process is attractive because it reduces the number of process units and thus construction costs. Over the last years, the process feasibility has been demonstrated in the bioreactor configurations mentioned above over a wide range of operational conditions including low pH values and high metal loads. Table 3.1 shows the configurations, operational conditions and results obtained in several sulphate-reducing bioreactors used for the treatment of metal containing-waste streams. The performance of these bioreactors has been evaluated mainly based on the COD and sulphate-removal efficiencies (%) as well as on the sulphate-reduction rates (g SO_4^{2-} reduced/L·d) upon variations of substrate, hydraulic retention time, temperature, influent pH, COD/SO_4^{2-} ratio and concentration and type of metals tested. It can be noticed that the substrate has a substantial impact on the sulphate and COD-removal efficiencies and on the sulphate-reduction rates. For instance, studies in an UAPBR using complex organic substrates have the lowest sulphate-reduction rates (0.06–0.47 g SO_4^{2-} reduced/L·d), while an UFBR and an DFBR, using lactate and ethanol as substrate, present the highest sulphate-reduction rates (2.6–4.6 g SO_4^{2-} reduced/L·d). In general, the studies presented in Table 3.1 report a fair performance despite the low pH and high removal efficiencies of the metals tested, which is higher than 80% in most cases (data not shown). This is partly due to the production of bicarbonate ions by the sulphate-reducing process and the sulphide present, which allow rising the pH and precipitate any metals upon introduction to the bioreactor.

A missing information in most of these studies is encountered in whether the metals could leave the system and be recovered, or if they accumulate within the bioreactor hampering long-term operation. Although the metals can be recovered from the metal sulphide-containing sludge (Tabak et al. 2003), this might imply biomass loss in the process leading to the reduction of the system performance.

Sulphate-reduction and metal recovery can be also performed in a multistage process consisting of: (1) a biological stage, separated from the precipitation stage (Hao 2000; Kaksonen and Puhakka 2007), (2) a biological stage and precipitation stage, separated from the settling stage (Hao 2000; Muyzer and Stams 2008) and (3) a biological stage separated from several precipitation settlers operating at different pH or sulphide concentration in order to achieve selective metal recovery (Veeken et al. 2003b; Esposito et al. 2006; König et al. 2006; Sampaio et al. 2009). In the last decade, these process configurations have been demonstrated for Cu and Zn at lab-scale (Foucher et al. 2001; Al-Tarazi et al. 2005a; Gramp et al. 2006; Esposito et al. 2006) and for Cu, Zn, As, Fe and Ni at full scale (Muyzer and Stams 2008). At full scale, the Nyrstar plant in The Netherlands treats a process water containing $ZnSO_4$, where sulphate-reduction takes place in a full-scale (500 m^3) gas lift reactor with hydrogen as electron donor (Muyzer and Stams 2008). Then the ZnS produced is collected in a settler and the excess sulphide is oxidized in an aerobic bioreactor. The process has also been assessed in a sulphate and metal-rich effluent coming from a coal process in South Africa and for the treatment of acid-mine drainage at the former Wheal Jane mine in Cornwall, UK (Paques 2016).

3.2.5 *Operational Conditions Affecting Sulphate-Reduction in Bioreactors*

3.2.5.1 Effect of pH

Although sulphate-reducing bacteria are naturally present in extreme pH environments (Muyzer and Stams 2008), optimal growth conditions in lab-scale are reported at pH values between 5.5 and 10 (Hao et al. 2014). Many studies have successfully demonstrated the application of the sulphate-reduction process for acid waste streams (2.5–3), since the process itself generates bicarbonate ions, which increase the waste stream pH up to 7.5–8.5 (Kaksonen and Puhakka 2007; Bekmezci et al. 2011). However, research on sulphate-reduction at acidophilic (pH below 7) (Ňancucheo and Johnson 2014) and alkaline (pH above 7) conditions (Sousa et al. 2015; Zhou and Xing 2015; Zhou et al. 2015) is still attractive for metal recovery purposes. This is because the manipulation of the pH in a wider range than neutral in bioreactors can allow selective precipitation, and thus selective recovery, of metals from multi metal streams (Huisman et al. 2006; Tabak et al. 2003) as metal sulphide solubility is pH dependent (Lewis 2010).

The effect of alkaline pH, accompanied with high salinity, on the sulphate-reduction process decreases the microbial growth rate and aggregation of biomass (Sousa et al. 2015). The effect of acidic pH on the sulphate-reduction process has been widely studied so it is known that the inhibition is caused by: (a) the increase in protons (H^+) (Sánchez-Andrea et al. 2014), (b) the formation of H_2S, which is the unionized sulphide-species (Reis et al. 1992; Hulshoff Pol et al. 1998; Hulshoff Pol et al. 2001; Willow and Cohen 2003; Lopes et al. 2007; Bijmans et al. 2008) and c) the formation of unionized organic acids (Kimura et al. 2006) either from organics added as electron donor, or those formed during the anaerobic degradation (e.g. acetate). The concentration of sulphide and acetate is a function of the pH due to chemical equilibrium (Fig. 3.2). Therefore, unionized acetate and sulphide concentration is higher at low pH values.

The inhibitory effect of H_2S and undissociated organic compounds relies on the ability to penetrate the cell membrane thus affecting the functioning of metabolic coenzymes and, denaturizing proteins (Kaksonen and Puhakka 2007). To avoid this, several operational strategies have been developed:

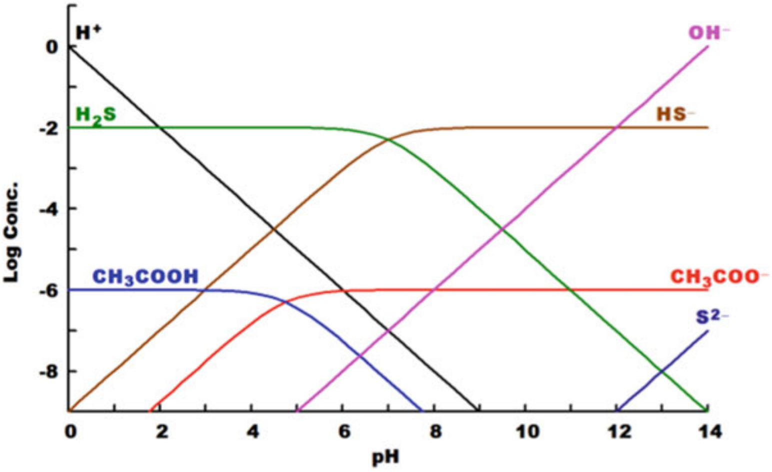


Fig. 3.2 Chemical speciation of aqueous sulphide and acetate as a function of pH. Diagram elaborated with the MEDUSA software (Puigdomènech 2010). Equilibrium values were taken from the HYDRA database at pKa 25 °C (Puigdomènech 2010) based on 10 mM of HS^- and CH_3COO^-

(a) The use of electron donors that do not form unionized organic acids, for instance, glycerol (Kimura et al. 2006; Ňancucheo and Johnson 2012), formate and hydrogen (Bijmans et al. 2010).
(b) Continuous sulphide-removal through N_2 stripping of the liquid media (Lopes et al. 2007; Bijmans et al. 2008).
(c) Recirculation of the effluent in order to dilute the sulphide concentration (Celis-García et al. 2007; Kaksonen et al. 2004).
(d) Sulphide-precipitation with metals (Hulshoff Pol et al. 2001; Kaksonen and Puhakka 2007), for example by Fe (Vakili et al. 2012).

3.2.5.2 Effect of Hydraulic Retention Time

Several studies have assessed the effect of the hydraulic retention time on the sulphate-reducing process with or without the presence of metals (Qinglin et al. 2012; Kaksonen et al. 2004; Dries et al. 1998; Mizuno et al. 1998; Nagpal et al. 2000; Alphenaar et al. 1993; Celis-García et al. 2007; Sahinkaya et al. 2009; Villa-Gómez et al. 2011; Villa Gómez et al. 2015). These experiments have been carried out by sudden or stepwise reduction of the hydraulic retention time. In every study, the term defined as “long” and “short” hydraulic retention time depends on the range used, type of bioreactor and operating conditions used. Regardless this, some generalizations on the effect of the hydraulic retention time in sulphate-reducing bioreactors can be made:

- A long hydraulic retention time (48 h) is applied at bioreactor start up to enhance biomass retention or immobilization within the bioreactor (Celis et al. 2009; Villa-Gómez et al. 2011).
- Depending on the electron donor used, methanogens or sulphate-reducing bacteria outcompete upon variations of the hydraulic retention time. For instance, acetate was used by sulphate-reducing bacteria at higher hydraulic retention times (40.2 h) when acetic acid (50%), propionic acid (40%) and sucrose (10%) was fed in a UASB/CSTR bioreactor, thus outcompeting methanogens (Alphenaar et al. 1993), while methanogens outcompeted sulphate-reducing bacteria in a GLR (55 °C) fed with CO when this bioreactor was operated at hydraulic retention times higher than 9 h (Sipma et al. 2007).
- Higher sulphate and COD removal efficiencies are achieved at long hydraulic retention times (Mizuno et al. 1998; Nagpal et al. 2000; Kaksonen et al. 2004; Celis-García et al. 2007; Sahinkaya et al. 2009; Sipma et al. 2007). However, substrate limitation can also occur (Nagpal et al. 2000), as biomass growth rate and electron donor/acceptor conversion rates overpass the electron donor/acceptor supply rate.
- Loss of biomass due to wash out is reported at short hydraulic retention times resulting in lower conversion rates due to low biomass concentration in the biroeactor (Dries et al. 1998; Kaksonen et al. 2004; Sipma et al. 2007; Villa Gómez et al. 2015; Alphenaar et al. 1993).

- Short hydraulic retention times can lead to low sulphide-production impeding total metal precipitation of metal-containing waste streams, thus allowing free metal toxicity (Villa Gómez et al. 2015).
- Due to faster growth rates of incomplete oxidizers as compared to complete oxidizers and acetotrophic sulphate-reducing bacteria, acetate accumulation has been reported at short hydraulic retention times (Nagpal et al. 2000; Kaksonen et al. 2004).

3.2.5.3 Effect of Metal Concentration

Metals can stimulate or inhibit sulphate-reducing bacteria depending on process-related factors such as pH, redox potential (Chen et al. 2008) and the reactive species in the mixed liquor (Labrenz et al. 2000; Gonzalez-Silva et al. 2009). These parameters drive the dissolved metal species concurrent with concentration. Dissolved metals can affect the sulphate-reducing bacteria metabolism by deactivating the enzymes and denaturing the proteins (Cabrera et al. 2006).

In sulphate-reducing bioreactors treating metal containing wastewaters, the sulphide reacts with metals forming insoluble metal sulphide particles, which reduces the metal toxicity and bioavailability (Kaksonen and Puhakka 2007). Despite this, inhibition of sulphate-reduction by insoluble metal sulphides can still occur (Gonzalez-Silva et al. 2009; Utgikar et al. 2004; Utgikar et al. 2002), particularly at pH values below neutral (Moosa and Harrison 2006; Reis et al. 1992) or if the metal sulphide-precipitation occurs onto the sulphate-reducing bacterial cells (Villa Gómez et al. 2015). Gonzalez-Silva et al. (2009) found that Cd (3 mM) precipitation with sulphide did not decrease the inhibition of cadmium on the sulphate-reduction process in a study investigating the inhibition effect of Fe, Cd and sulphide on the substrate utilization rate of sulphate-reducing granular sludge in a UASB bioreactor.

3.3 Metal Sulphide-Precipitation Process

3.3.1 Formation of Metal Sulphide Precipitates

Besides the bioreactor configuration and the number of stages in the treatment process, metal sulphide-precipitation itself is a complex process that needs to be understood for optimal metal recovery. The kinetic phenomena associated with metal sulphide-precipitation are nucleation, and crystal growth (Fig. 3.3). The driving force of both phenomena is the supersaturation. The supersaturation level is the amount by which the solute concentration exceeds the saturation concentration. Crystallization only occurs if the system is supersaturated (Larsen et al. 2006). In general, high supersaturation levels favour nucleation, thus to produce large

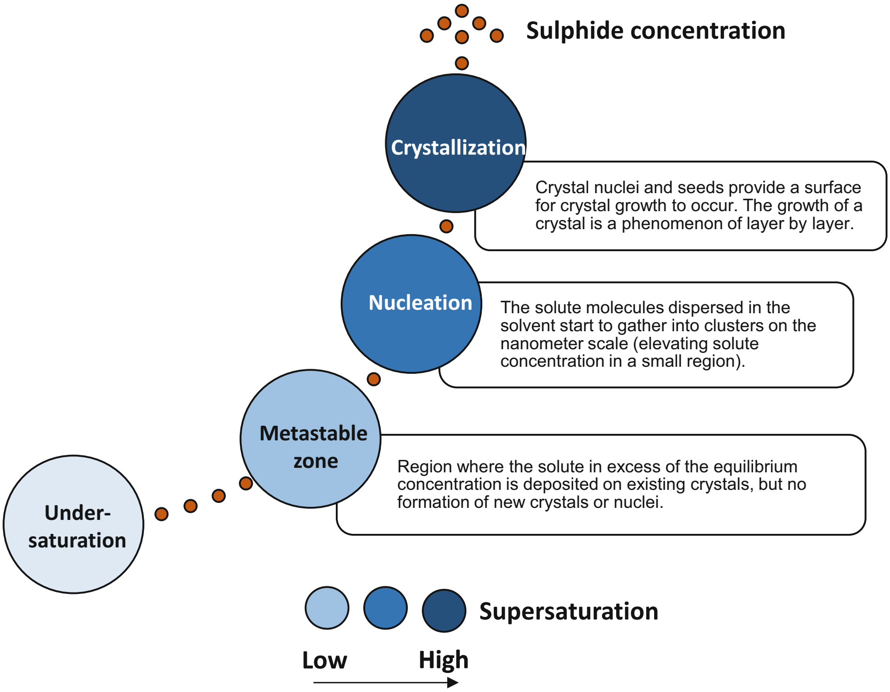


Fig. 3.3 Schematic representation of the saturation zones driven by the sulphide concentration, where nucleation and crystallization occur

particles the supersaturation should be minimized. The supersaturation level σ for metal sulphides can be expressed in terms of the solubility product (Veeken et al. 2003a):

$$\sigma = \sqrt{\frac{\left(Me^{2+}\right)\left(S^{2-}\right)}{K_{sp}}}$$

Where σ is the supersaturation level, (Me^{2+}) is metal activity (mol/L), (S^{2-}) is sulphide activity (mol/L). Later agglomeration and break up of crystals also occur.

At high levels of supersaturation both phenomena compete for the available solute (metal and sulphide). Depending on the conditions, either nucleation or crystal growth may be predominant over the other, and as a result, crystals with different sizes and shapes are obtained (Mersmann 1999).

Metal sulphide precipitates have a low solubility (Fig. 3.4), as a consequence, the supersaturation is high (Hammack et al. 1994) and difficult to control, especially at the feeding points (Lewis and van Hille 2006) due to micro mixing limitations (Tabak and Govind 2003). This results in the formation of small particles, called fines, which are difficult to recover (Mokone et al. 2010; Villa-Gómez et al. 2011). This scenario has been observed in bioreactors as well (Villa-Gómez et al. 2011).

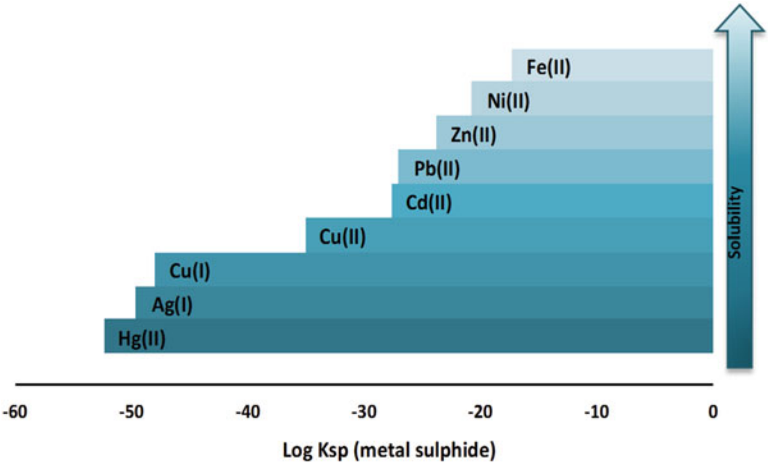


Fig. 3.4 Solubility product constants (K_{sp}) of metal (Me^{x+}) sulphides (S^{2-}) at standard conditions (25 °C, 1 atm) (Data from Sampaio et al. 2009)

3.3.1.1 Solubility Product

The solubility product determines whether a metal sulphide will stay dissolved or will precipitate. For a solid precipitate of metal sulphide $M_xS_y(s)$, the following general solubility expression can be written:

$$M_xS_y(s) \leftrightarrow xM^{2+} + yS^{2-}$$

The solubility product (K_{sp}) of the metal sulphide is defined as:

$$K_{sp} = [M^{2+}]^x[S^{2-}]^y$$

Where Ksp is in mol^2/L^2 when $x = y = 1$, $[M^{2+}]$ is the equilibrium activity of metal ion M^{2+} (mol/L) and $[S^{2-}]$ is the equilibrium activity of S^{2-} (mol/L) (Sampaio et al. 2009).

Several authors have found that the metal sulphide-precipitation rate is ruled by the sulphide concentration by means of the solubility product (Bryson and Bijsterveld 1991; Mishra and Das 1992; Lewis and Swartbooi 2006; Veeken et al. 2003b). Veeken et al. (2003b) showed the different precipitation rates of Cd, Cu, Ni, Pb and Zn upon the variations of the sulphide concentration expressed in the logarithm of the S^{2-} species (pS) at a fixed pH of 6. Based on this principle, selective precipitation of individual metals has been demonstrated in additional stages by controlling the pH and pS (Veeken et al. 2003a; Esposito et al. 2006; König et al. 2006; Sampaio et al. 2009).

Many studies on metal sulphide precipitation have focused on studying the way to reduce the high level of supersaturation on the metal sulphide precipitation in order to increase the size of the precipitates for better solid-liquid separation. Van Hille et al. (2005) studied the influence of the sulphide to Cu molar ratio, recycle flow rate, inlet Cu flow rate and the inlet Cu concentration on the Cu conversion and removal efficiency. They found that the sulphide to Cu molar ratio and the bisulfide ion formation were the most important factors determining local supersaturation. Al-Tarazi (2005b) used gaseous H_2S as precipitating reagent for Cu and Zn to reduce the high level of supersaturation in a bubble column and concluded that the morphology of the metal sulphide precipitates was more favourable than that of the precipitates produced using an aqueous sulphide source.

Some studies have shown the influence of the geometry and operating conditions of the precipitator reactor on the crystallization process. For instance, Al-Tarazi et al. (2005b) studied the effects of the configuration on three different types of reactors for the precipitation of Zn and Cu: laminar jet, bubble column and a Mixed Solution Mixed Product Removal (MSMPR) reactor, studying the effects of mass transfer and process conditions on the morphology of the produced crystals. They found that the largest crystals of metal sulphides were obtained at high supersaturation conditions, moderate stirrer speeds, short residence times, a pH value of around 5 and high Cu^{2+} to sulphide ratios. Sampaio et al. (2009) observed that the particle size of CuS in a continuously stirred tank reactor increased if allowed to settle (from 36 to 180 μm), whereas upon vigorously stirring, the particles decreased to below 3 μm.

In addition to the influence of geometry and operating conditions, foreign particles determine the particle size of the metal sulphides by affecting the relative rates of nucleation and crystal growth (Mersmann 1999). Gramp et al. (2006) showed the differences between biogenic and abiotic sulphide used to precipitate copper in cultures of sulphate-reducing bacteria and Na_2S solutions. They found that bacterial cells alter crystal formation by inhibiting particle nucleation and as a consequence the chemically produced covellite (CuS) should be more resistant to biogeochemical oxidation as compared to poorly crystalline biogenic Cu-sulphide. Contrary to the previous authors, Bijmans et al. (2009c) suggested that the biomass functioned as nucleation seeds, enhancing crystal growth, reporting NiS precipitates formed with biogenic sulphide ranging from 13 to 73 μm.

3.3.2 Factors Affecting Metal Sulphide Precipitation

3.3.2.1 pH

The pH has an influence on the speciation of the components present in the liquid phase of bioreactors, which affects metal sulphide precipitation. Villa-Gómez et al. (2014b) studied the morphology, mineralogy, and solid-liquid phase separation of the Cu and Zn precipitates formed with biogenic sulphide at pH 3, 5, and 7. They found that at pH 5, the dissolved organic matter present in the bioreactor liquor

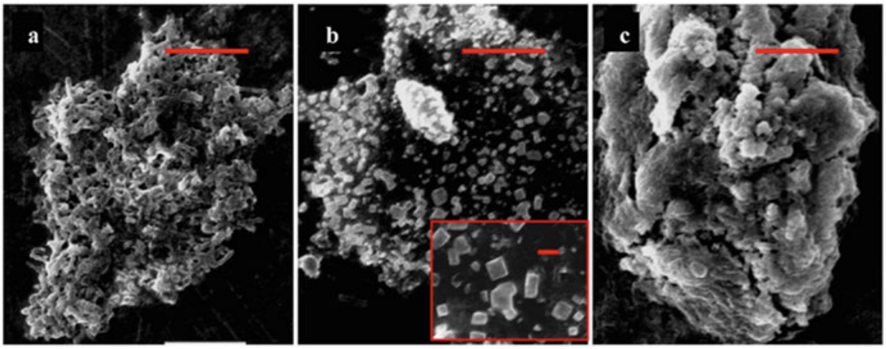


Fig. 3.5 Scanning electron microscopy images of the precipitates formed at pH 7 (**a**), pH 5 (**b**) and pH 3 (**c**) with biogenic sulphide and metals (Zn, Cu) at 10 µm magnification (zoomed picture **b** at 1 µm magnification) (Source: Villa-Gómez et al. 2014b)

induced crystallization and hampered agglomeration of the metal sulphides, while at pH 7 and 3, the agglomeration phenomena were clearly predominant (Fig. 3.5).

The pH-dependent solubility of the metal sulphides has been used to selectively recover metals from complex and simple mixed metal systems (Tokuda et al. 2008; Bijmans et al. 2009c; Sahinkaya et al. 2009; Tabak et al. 2003). Foucher et al. (2001) found that Cu and Zn sulphides could be selectively recovered at pH 2.8 and 3.5, while Ni and Fe sulphides could only be removed (not recovered) at pH 6. Similar results were found by Sampaio et al. (2009), who selectively precipitated CuS (covellite) at pH 2 and 3 and ZnS (sphalerite) at pH 3 and 4. Sampaio et al. (2010) additionally demonstrated that Ni can be selectively recovered from a Ni-Fe solution at pH 5 using a single stage bioreactor operating at low pH. The results also suggested that the pH should be lower than 4.8 for complete Ni-Fe separation.

3.3.3 Competing Metal Removal Mechanisms

Although the low solubility of metal sulphides favour metal removal mechanism (Fig. 3.4), other precipitation reactions can also occur in sulphate-reducing bioreactors. Several authors have confirmed alternative precipitates are formed at low sulphide concentrations, particularly for metals with higher solubility such as Zn (Mokone et al. 2010; Neculita et al. 2007; Villa-Gómez et al. 2012). Although the decrease of supersaturation is preferable for crystal growth (Fig. 3.3), it also allows the formation of alternative precipitates such as brochantite ($Cu_4(OH)_6SO_4$) (Mokone et al. 2010), Zn-phosphate (Villa-Gómez et al. 2012) and hydroxides (Samaranayake et al. 2002; Neculita et al. 2008). Other metal removal mechanisms that can occur in bioreactors include: biosorption as well as sorption onto previously formed metal sulphide precipitates (Neculita et al. 2007; Villa-Gómez et al. 2012; Villa-Gómez et al. 2014b; van Hullebusch et al. 2003).

Elucidation of the metal removal mechanisms that can occur apart from metal sulphide precipitation in bioreactors is difficult, as the solid phase techniques used for the identification of the chemical species are limited to scanning electron microscopy and X-ray diffraction, which display low resolution on poorly crystallized samples immersed in biological tissues (Neculita et al. 2007). Various studies have addressed different metal removal mechanisms based on chemical equilibrium calculations to predict the species formed in bioreactors (Bartacek et al. 2008; Villa-Gómez et al. 2012, 2015). Despite being a great help to understand the chemical speciation, these are based on the formation of species at thermodynamic equilibrium, which is not always reached in bioreactors.

X-ray absorption spectroscopy, which consists of two complementary techniques, X-ray absorption near edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS), is an accurate technique for the analysis of metals in biological samples (Prange and Modrow 2002; van Hullebusch et al. 2009; Lenz et al. 2011; Shakeri Yekta et al. 2012; Villa-Gómez et al. 2012, 2014b). This technique was applied by Villa-Gómez et al. (2014b) to identify the Cu and Zn removal mechanisms in sulphate-reducing bioreactors. Figure 3.6 shows Zn K-edge XANES spectra of the Zn precipitates obtained when the metals were put in contact with biogenic sulphide at pH 3, 5 and 7. The spectroscopic similarities with sphalerite were the highest at pH 5, where XANES features A to E were almost identical, while at pH 3, these features were in a lesser extent similar. In contrast, the features A and E at pH 7 indicated a contribution from another Zn environment, where the feature E was slightly shifted towards lower energies, thus suggesting the

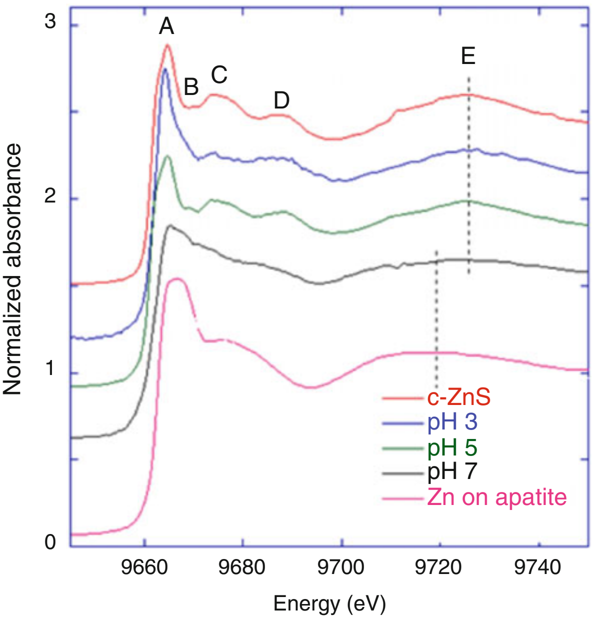


Fig. 3.6 Zn K-edge XANES spectra for selected model compounds (c-ZnS and Zn sorbed on apatite) as compared to the sulphide precipitates formed in three batch samples of the study of Villa-Gómez et al. (2014b)

presence of minor amounts of Zn-O, as in Zn-sorbed hydroxyapatite, Zn: $Ca_5(PO_4)_3$•(OH).

3.4 Modelling and Control of the Sulphate-Reduction Process for Metal Recovery

3.4.1 Modelling

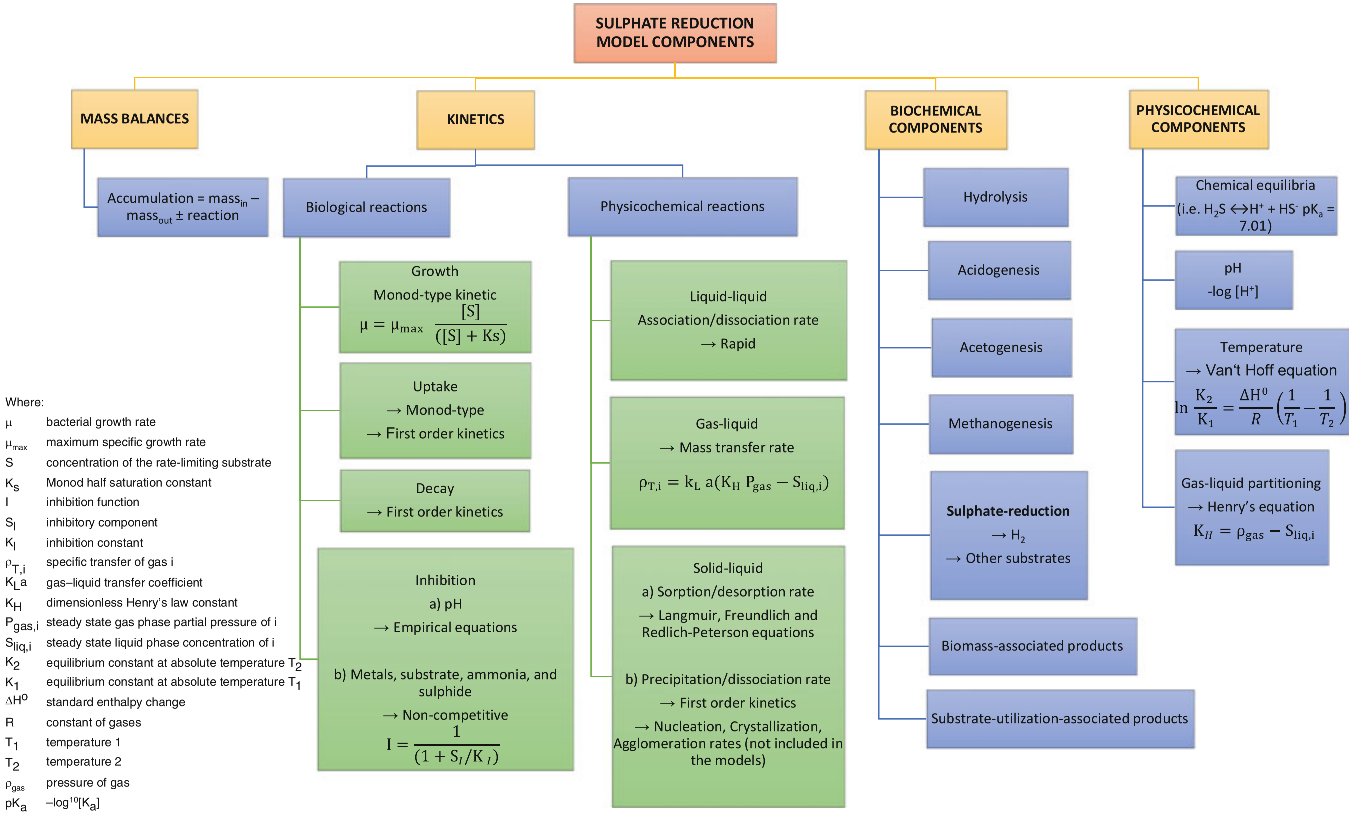
Mathematical modelling is a powerful tool for process analysis and design. It also forms the basis for monitoring and control schemes of bioreactors. The baseline for modelling anaerobic digestion systems, including sulphate-reduction, is the anaerobic digestion model no. 1 (ADM1), developed by the IWA task group (Batstone et al. 2002). It comprehends mass balances, kinetics, biochemical and physicochemical components (Batstone 2006). Further extensions of sulphate-reduction modelling include additions in kinetics, biochemical and physicochemical components (Cassidy et al. 2015; Barrera et al. 2015). Sulphate-reduction modelling has been developed in several bioreactor configurations to predict sulphide inhibition/toxicity, microbial competition, kinetic parameters, biofilm or granulation development (Cassidy et al. 2015), sulphide equilibrium (Barrera et al. 2015) and for scale-up design (Tabak and Govind 2003).

3.4.1.1 Model Components

Figure 3.7 shows the basic components of sulphate-reduction models. These components are interrelated and depend on each other. Thus, mass balances, which describe accumulation and reaction within a system in relation to flow across the system boundaries for each component involved in the system (Batstone 2006), require the rate of the biological and physicochemical reactions that can occur in the system to predict the final concentrations of each component.

3.4.1.1.1 Kinetics

Biological reactions include growth, uptake, decay and inhibition of microorganisms. The growth rate and uptake rate of electron donor/acceptor are most commonly described by Monod (or Michaelis-Menten) kinetics, while decay rates are better expressed by first order kinetics (Batstone 2006). Inhibition is also included within the biological reactions as it may have a strong effect on biochemical processes by decreasing the conversion or growth rate, thus affecting the overall performance. In sulphate-reducing bioreactors, pH, metals, substrate, ammonia, and sulphide mainly induce inhibition. Commonly, inhibition increases with an



Where:

μ	bacterial growth rate
μ_{max}	maximum specific growth rate
S	concentration of the rate-limiting substrate
K_S	Monod half saturation constant
I	inhibition function
S_I	inhibitory component
K_I	inhibition constant
$\rho_{T,i}$	specific transfer of gas i
$K_L a$	gas–liquid transfer coefficient
K_H	dimensionless Henry's law constant
$P_{gas,i}$	steady state gas phase partial pressure of i
$S_{liq,i}$	steady state liquid phase concentration of i
K_2	equilibrium constant at absolute temperature T_2
K_1	equilibrium constant at absolute temperature T_1
ΔH^O	standard enthalpy change
R	constant of gases
T_1	temperature 1
T_2	temperature 2
ρ_{gas}	pressure of gas
pK_a	$-\log^{10}[K_a]$

Fig. 3.7 Flow diagram presenting the main components of the sulphate-reduction models

increase in the inhibitor concentration, leading to a gradual decrease in the specific substrate utilization rate (Cassidy et al. 2015). Inhibition by pH is implemented through empirical equations when both high and low pH inhibition occur, or when only low pH inhibition occurs (Batstone et al. 2002). Inhibition due to metals substrate, ammonia and sulphide are most commonly represented by non-competitive functions (Batstone et al. 2002; Cassidy et al. 2015). This function has been used to study the inhibition by Fe, Cd and sulphide in a UASB bioreactor (Gonzalez-Silva et al. 2009) and by sulphide in an up-flow fluidized bed bioreactor (Kaksonen et al. 2004).

3.4.1.1.2 Physicochemical Components

Physicochemical reactions are defined as those not mediated by microorganisms, and include (Fig. 3.5): (a) liquid-liquid reactions, (b) gas-liquid exchanges, (c) -liquid-solid transformations. Liquid-liquid reactions, comprehending ion association/dissociation, are acknowledge in anaerobic digestion models but, since they occur at a relatively rapid scale (Batstone et al. 2002), the reaction rates are omitted. Gas-liquid transformations have been mainly described for CH_4, CO_2 and H_2 and less often for sulphide. Barrera et al. (2015) presented an extension of the ADM1 with sulphate- reduction for a very high strength and sulphate-rich wastewater where the concentrations of total aqueous, free and gas phase sulphides were accurately predicted.

Physicochemical components include chemical equilibrium, pH, temperature and gas-liquid partitioning. Chemical equilibrium such as acid-base equilibrium for inorganic carbon and nitrogen, acetate, propionate, valerate, butyrate and hydrogen is either by formulation of the base or acid concentration or by calculation of the equilibrium in algebraic equations (Lauwers et al. 2013). pH calculation involves solving a set of algebraic or differential equations to calculate the concentrations of ionic acids and bases related with ionic, active concentration state variables (Batstone 2006). Changes in temperature have a fundamental influence on the physicochemical system, mainly because of changes in equilibrium constants, for this, the most widely used is the Van't Hoff equation (IWA 2002). The main components considered in gas-liquid partitioning are CO_2, CH_4, H_2 and H_2S. When the liquid phase is relatively dilute, Henry's law can be used to describe the equilibrium relationship (IWA 2002).

Liquid-solid reactions include sorption/desorption and precipitation/solubilisation mechanisms. These have been less studied and are not included in the ADM1 (IWA 2002). Sorption/desorption mechanisms are highly relevant when metals are present in bioreactors. These are mainly attributed to an ion exchange mechanism on the surface of the biomass (van Hullebusch et al., 2003) or by extracellular polymers (van Hullebusch et al. 2005; Liu et al. 2015). Metal sorption mechanisms in the anaerobic granular sludge have been described, aside of the overall bioreactor system, with Langmuir, Freundlich and Redlich-Peterson equations (van Hullebusch et al. 2004, 2005, 2006; Pat-Espadas et al. 2016).

Precipitation/solubilisation mechanisms are mainly important in bioreactors where sulphate-reduction occurs for metal sulphide precipitation. The simple method to include them is an equilibrium reaction or simple first order kinetics (Parker and Wu 2006; IWA 2002). This can be fairly valid as the solubility product coefficients for metal sulphide precipitates are extremely small, thus reacting fast. Parker and Wu (2006) introduced a first-order metal sulphide rate coefficient (arbitrarily) of 10^6 M/d in a modified ADM1 to describe the effect of metal sulphide precipitation in the formation and emission of odorous compounds in anaerobic sludge digestion. The model was capable to predict the changes in emissions of H_2S upon variations of metal concentrations due to metal sulphide precipitation.

It is important to stress that the precipitation process comprises: nucleation, and crystallization, and the predominance of one of these defines the size of the metal sulphide precipitates and thus the suitability of metal recovery in bioreactors. As the predominance of one mechanism over another is influenced by the sulphide concentration and pH, these mechanisms should, therefore, be considered in the modelling of sulphate-reducing bioreactors. The metal precipitation process has been modelled separately from the sulphate-reducing process in completely stirred tank reactors to obtain crystallization kinetics (Al-Tarazi et al. 2004) to predict the effects of organic substances and sulphide concentration (König et al. 2006), pH variation (Luptakova and Kusnierova 2005; König et al. 2006; Sampaio et al. 2009) and metal concentration (König et al. 2006), and to design an adequate control strategy to estimate the effluent metal concentration (Sampaio et al. 2009). This knowledge could be the start point to incorporate the precipitation mechanisms in sulphate-reduction models.

3.4.1.1.3 Biochemical Components

Biochemical components include the stoichiometric microbial degradation pathways hydrolysis, acidogenesis, acetogenesis and methanogenesis (Fig. 3.1) and sulphate-reduction as well as biomass-associated products and substrate-utilization-associated products (Batstone et al. 2002). Sulphate-reduction, regardless the electron donor used, has been generalized in one component, as some models consider only the oxidation of the available hydrogen (Batstone, 2006) or from other substrates such as volatile fatty acids directly by sulphate-reducing bacteria (Barrera et al. 2015; Fedorovich et al. 2003). The biomass-associated products and substrate-utilization-associated products have been recently introduced in sulphate-reduction models to understand the onset of sulphate-reduction in denitrifying membrane biofilm reactors (Tang et al. 2013) and to determine the impact of sulphate and polyhydroxybutyrate-accumulation on process control of sulphate-reducing bioreactors (Cassidy et al. 2017).

3.4.2 Control and Automation

As mentioned before, metal precipitation/recovery is highly dependent on the sulphide concentration and pH. Therefore, control and automation of sulphate-reducing bioreactors are inherently essential to achieve metal recovery in bioreactors. Additionally, industrial and mining wastewaters are deficient in organic compounds as electron donor source for sulphate-reduction. Thus, for practical implementation, steering the sulphide-production towards its required stoichiometric amount in bioreactors is highly relevant to avoid unnecessary electron donor addition and over production of sulphide (Villa-Gómez et al. 2014a).

The basic components of a control system are: (i) the process (sulphate-reducing bioreactor), (ii) the measurement device (sensors) for process monitoring and iii) the controller (Fig. 3.8). A control system requires monitoring of the process to increase knowledge on the process, and thus, to design an adequate control strategy (Cassidy et al. 2015). Advances in instrumentation have enabled the on-line monitoring of critical parameters for early detection of process disturbances (Nguyen et al. 2015). Online sensors such as pH, oxygen redox potential and ion selective electrodes have been used for the measurement of crucial variables in the sulphate-reducing process (Villa-Gómez et al. 2014a; Torner-Morales and Buitrón 2010). An oxygen, redox potential sensor and pH electrode were used to maintain sulphate-reduction/sulphide oxidation in a single sequencing batch reactor with a significant yield of 64% of elemental sulphur (Torner-Morales and Buitrón 2010). A S^{2-} selective electrode was used for sulphide monitoring in a down-flow fluidized bed bioreactor for the design of a control strategy to control the sulphide production in sulphate-reducing bioreactors (Villa-Gómez et al. 2014a, b). Other

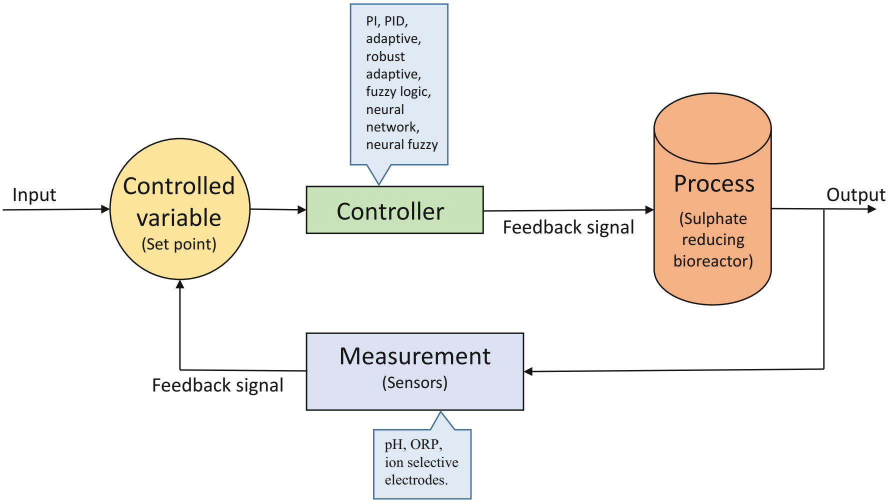


Fig. 3.8 Basic components of a control system applied to sulphate-reducing bioreactors. *PI* proportional integral, *PID* proportional integral derivative, *ORP* oxygen redox potential

sensors such as SO_4^{2-} selective electrodes, not yet tested in the sulphate-reduction process, could be potentially useful for process control of these systems (Cassidy et al. 2015).

Once the sensor has sent the data, the controller, can decide the output applied to the manipulated variable. The controllers used in anaerobic digestion systems, with scarce contribution to sulphate-reducing systems, include proportional integral (PI) control, PI derivative (PID) control, adaptive control, robust adaptive, fuzzy logic, neural network, and neural fuzzy (Nguyen et al. 2015). In the anaerobic digestion process, these controllers have been used to steer the feeding rate, volatile fatty acid concentration, pH, bicarbonate alkalinity, biogas and methane production rate (Pind et al. 2003; Nguyen et al. 2015), while for sulphate-reduction, only the pH has successfully been controlled with commercially available pH controllers especially designed for bioreactors (Bijmans et al. 2009a; Bijmans et al. 2010).

A first approach towards the control of the sulphide concentration in a sulphate-reducing bioreactor for metal precipitation/recovery was studied by Villa-Gómez et al. (2014a). Step changes in the organic loading rate were applied by changing the lactate concentration or the hydraulic retention time, and the sulphide concentration and pH were measured using pS and pH electrodes connected to the LabView software version 2009®. The pS output values resulting from both control strategies were used to determine the PID parameters. Despite that the controller was not tested, the knowledge gained on the critical factors affecting sulphide control in bioreactors put the automation of these systems one step further, not only for metal recovery but also for other biotechnological applications where biological sulphide production control is required.

3.5 Conclusion

This chapter overviewed the factors affecting metal recovery in sulphate-reducing bioreactors. Different bioreactor configurations have been applied for sulphate-reduction and metal precipitation. However, metal recovery cannot always be achieved in these bioreactors, since metals precipitate partly in the biomass, which hampers metal recovery. Many mining and metallurgical waste streams are deficient in organic compounds as electron donor for sulphate-reduction, thus, cheap electron donors and steering the sulphide production towards its required stoichiometric amount in bioreactors is highly relevant to avoid unnecessary electron donor addition and overproduction of sulphide. Process control in sulphate-reducing bioreactors is essential to align the sulphide production to the amount of metals desired to precipitate.

References

Alphenaar AP, Visser A, Lettinga G (1993) The effect of liquid upward velocity and hydraulic retention time on granulation in UASB reactors treating wastewater with a high sulphate content. Bioresour Technol 43(3):249–258. doi:10.1016/0960-8524(93)90038-D

Al-Tarazi M, Heesink ABM, Azzam MOJ, Yahya SA, Versteeg GF (2004) Crystallization kinetics of ZnS precipitation; an experimental study using the mixed-suspension-mixed-product-removal (MSMPR) method. Cryst Res Technol 39(8):675–685. doi:10.1002/crat.200310238

Al-Tarazi M, Heesink ABM, Versteeg GF, Azzam MOJ, Azzam K (2005) Precipitation of CuS and ZnS in a bubble column reactor. AICHE J 51(1):235–246. doi:10.1002/aic.10310

Al-Tarazi M, Heesink ABM, Versteeg GF (2005) Effects of reactor type and mass transfer on the morphology of CuS and ZnS crystals. Cryst Res Technol 40(8):735–740. doi:10.1002/crat.200410421

Barrera EL, Spanjers H, Solon K, Amerlinck Y, Nopens I, Dewulf J (2015) Modeling the anaerobic digestion of cane-molasses vinasse: extension of the anaerobic digestion model no. 1 (ADM1) with sulfate reduction for a very high strength and sulfate rich wastewater. Water Res 71:42–54. doi:10.1016/j.watres.2014.12.026

Bartacek J, Fermoso F, Baldó-Urrutia A, van Hullebusch E, Lens P (2008) Cobalt toxicity in anaerobic granular sludge: influence of chemical speciation. J Ind Microbiol Biotechnol 35 (11):1465–1474. doi:10.1007/s10295-008-0448-0

Batstone DJ (2006) Mathematical modelling of anaerobic reactors treating domestic wastewater: rational criteria for model use. Rev Environ Sci Biotechnol 5(1):57–71. doi:10.1007/s11157-005-7191-z

Batstone DJ, Keller J, Angelidaki I, Kalyuzhnyi SV, Pavlostathis SG, Rozzi A, Sanders WT, Siegrist H, Vavilin VA (2002) The IWA Anaerobic Digestion Model No 1 (ADM1). Water Sci Technol 45(10):65–73

Bekmezci OK, Ucar D, Kaksonen AH, Sahinkaya E (2011) Sulfidogenic biotreatment of synthetic acid mine drainage and sulfide oxidation in anaerobic baffled reactor. J Hazard Mater 189 (3):670–676. doi:10.1016/j.jhazmat.2011.01.087

Bijmans MFM, Dopson M, Ennin F, Lens PNL, Buisman CJN (2008) Effect of sulfide removal on sulfate reduction at pH 5 in a hydrogen fed gas-lift bioreactor. J Microbiol Biotechnol 18 (11):1809–1818. doi:10.4014/jmb.0800.109

Bijmans MF, Dopson M, Peeters TW, Lens PN, Buisman CJ (2009a) Sulfate reduction at pH 5 in a high-rate membrane bioreactor: reactor performance and microbial community analyses. J Microbiol Biotechnol 19(7):698–708

Bijmans MFM, van Helvoort P-J, Buisman CJN, Lens PNL (2009b) Effect of the sulfide concentration on zinc bio-precipitation in a single stage sulfidogenic bioreactor at pH 5.5. Sep Purif Technol 69(3):243–248

Bijmans MFM, van Helvoort P-J, Dar SA, Dopson M, Lens PNL, Buisman CJN (2009c) Selective recovery of nickel over iron from a nickel-iron solution using microbial sulfate reduction in a gas-lift bioreactor. Water Res 43(3):853–861. doi:10.1016/j.watres.2008.11.023

Bijmans MFM, de Vries E, Yang C-H, N Buisman CJ, Lens PNL, Dopson M (2010) Sulfate reduction at pH 4.0 for treatment of process and wastewaters. Biotechnol Prog 26 (4):1029–1037. doi:10.1002/btpr.400

Bijmans MFM, Buisman CJN, Meulepas RJW, Lens PNL (2011) 6.34 – Sulfate reduction for inorganic waste and process water treatment. In: Murray M-Y (ed) Comprehensive biotechnology, 2nd edn. Academic Press, Burlington, pp 435–446. doi:10.1016/B978-0-08-088504-9.00471-2

Boonstra J, van Lier R, Janssen G, Dijkman H, Buisman CJN (1999) Biological treatment of acid mine drainage. Proc Metal 9B:559–567. doi:10.1016/S1572-4409(99)80145-X

Borja PR, Colmenarejo Morcillo MF, Durán-Barrantes MM, Jiménez-Rodríguez AM, Raposo Bejines F, Sánchez E (2010) Biological sulphate removal in acid mine drainage using anaerobic fixed bed reactors with cheese whey as a carbon source. Latin American Appl Res 335:329–335

Brooks CS (1991) Metal recovery from industrial wastes. Lewis Publishers Inc., Chelsea. doi:10.1007/BF03258716

Bryson AW, Bijsterveld CH (1991) Kinetics of the precipitation of manganese and cobalt sulphides in the purification of a manganese sulphate electrolyte. Hydrometallurgy 27 (1):75–84. doi:10.1016/0304-386X(91)90079-2

Cabezas A, de Araujo J, Callejas C, Galès A, Hamelin J, Marone A, Sousa D, Trably E, Etchebehere C (2015) How to use molecular biology tools for the study of the anaerobic digestion process? Rev Environ Sci Bio/Technol 14(4):555–593. doi:10.1007/s11157-015-9380-8

Cabrera G, Pérez R, Gómez JM, Ábalos A, Cantero D (2006) Toxic effects of dissolved heavy metals on *Desulfovibrio vulgaris* and *Desulfovibrio* sp. strains. J Hazard Mater 135 (1–3):40–46. doi:10.1016/j.jhazmat.2005.11.058

Caldwell SL, Laidler JR, Brewer EA, Eberly JO, Sandborgh SC, Colwell FS (2008) Anaerobic oxidation of methane: mechanisms, bioenergetics, and the ecology of associated microorganisms. Environ Sci Technol 42(18):6791–6799. doi:10.1021/es800120b

Cassidy J, Lubberding HJ, Esposito G, Keesman KJ, Lens PN (2015) Automated biological sulphate reduction: a review on mathematical models, monitoring and bioprocess control. FEMS Microbiol Rev 39(6):823–853. doi:10.1093/femsre/fuv033

Cassidy J, Frunzo L, Lubberding HJ, Villa-Gómez DK, Esposito G, Keesman KJ, Lens PNL (2017) Role of microbial accumulation in biological sulphate reduction using lactate as electron donor in an inversed fluidized bed bioreactor: operation and dynamic mathematical modelling. Int Biodeterior Biodegrad 121:1–10. doi:http://dx.doi.org/10.1016/j.ibiod.2017.03.006

Celis L, Villa-Gómez D, Alpuche-Solís A, Ortega-Morales B, Razo-Flores E (2009) Characterization of sulfate-reducing bacteria dominated surface communities during start-up of a down-flow fluidized bed reactor. J Ind Microbiol Biotechnol 36(1):111–121. doi:10.1007/s10295-008-0478-7

Celis-García LB, Razo-Flores E, Monroy O (2007) Performance of a down-flow fluidized bed reactor under sulfate reduction conditions using volatile fatty acids as electron donors. Biotechnol Bioeng 97(4):771–779. doi:10.1002/bit.21288

Chang IS, Shin PK, Kim BH (2000) Biological treatment of acid mine drainage under sulphate-reducing conditions with solid waste materials as substrate. Water Res 34(4):1269–1277. doi:10.1016/S0043-1354(99)00268-7

Chen Y, Cheng JJ, Creamer KS (2008) Inhibition of anaerobic digestion process: a review. Bioresour Technol 99(10):4044–4064. doi:10.1016/j.biortech.2007.01.057

Costa MC, Santos ES, Barros RJ, Pires C, Martins M (2009) Wine wastes as carbon source for biological treatment of acid mine drainage. Chemosphere 75(6):831–836. doi:10.1016/j.chemosphere.2008.12.062

Dar S, Bijmans M, Dinkla I, Geurkink B, Lens P, Dopson M (2009) Population dynamics of a single-stage sulfidogenic bioreactor treating synthetic zinc-containing waste streams. Microb Ecol 58(3):529–537. doi:10.1007/s00248-009-9509-9

Deng D, Lin L-S (2013) Two-stage combined treatment of acid mine drainage and municipal wastewater. Water Sci Technol 67(5):1000–1007. doi:10.2166/wst.2013.653

Deng D, Weidhaas JL, Lin L-S (2016) Kinetics and microbial ecology of batch sulfidogenic bioreactors for co-treatment of municipal wastewater and acid mine drainage. J Hazard Mater 305:200–208. doi:10.1016/j.jhazmat.2015.11.041

Dijkman H, Buisman CJN, Bayer HG (1999) Biotechnology in the mining and metallurgical industries: cost savings through selective precipitation of metal sulfides. In: Young DBD SK, Hackl RP, Dixon DG (ed) Copper 99 – Cobre 99 International Conference, Vol. IV: Hydrometallurgy of Copper 1999 phoenix, Arizona, USA. The minerals, metals & materials society, Warrendale, Pennsylvania, USA, 10–13 Oct 1999, pp 113–126

Dries J, De Smul A, Goethals L, Grootaerd H, Verstraete W (1998) High rate biological treatment of sulfate-rich wastewater in an acetate-fed EGSB reactor. Biodegradation 9(2):103–111. doi:10.1023/a:1008334219332

Esposito G, Veeken A, Weijma J, Lens PNL (2006) Use of biogenic sulfide for ZnS precipitation. Sep Purif Technol 51(1):31–39. doi:10.1016/j.seppur.2005.12.021

Fedorovich V, Lens P, Kalyuzhnyi S (2003) Extension of Anaerobic digestion model no. 1 with processes of sulfate reduction. Appl Biochem Biotechnol 109(1–3):33–45. doi:10.1385/ABAB:109:1-3:33

Foucher S, Battaglia-Brunet F, Ignatiadis I, Morin D (2001) Treatment by sulfate-reducing bacteria of Chessy acid-mine drainage and metals recovery. Chem Eng Sci 56 (4):1639–1645. doi:10.1016/S0009-2509(00)00392-4

Gallegos-Garcia M, Celis LB, Rangel-Méndez R, Razo-Flores E (2009) Precipitation and recovery of metal sulfides from metal containing acidic wastewater in a sulfidogenic down-flow fluidized bed reactor. Biotechnol Bioeng 102(1):91–99. doi:10.1002/bit.22049

Gibert O, de Pablo J, Luis Cortina J, Ayora C (2004) Chemical characterisation of natural organic substrates for biological mitigation of acid mine drainage. Water Res 38(19):4186–4196. doi:10.1016/j.watres.2004.06.023

Gonzalez-Silva BM, Briones-Gallardo R, Razo-Flores E, Celis LB (2009) Inhibition of sulfate reduction by iron, cadmium and sulfide in granular sludge. J Hazard Mater 172(1):400–407. doi:10.1016/j.jhazmat.2009.07.022

Gramp JP, Sasaki K, Bigham JM, Karnachuk OV, Tuovinen OH (2006) Formation of covellite (CuS) under biological sulfate-reducing conditions. Geomicrobiol J 23(8):613–619. doi:10.1080/01490450600964383

Hammack RW, Edenborn HM (1992) The removal of nickel from mine waters using bacterial sulfate reduction. Appl Microbiol Biotechnol 37(5):674–678. doi:10.1007/bf00240748

Hammack RW, Edenborn HM, Dvorak DH (1994) Treatment of water from an open-pit copper mine using biogenic sulfide and limestone: a feasibility study. Water Res 28(11):2321–2329. doi:10.1016/0043-1354(94)90047-7

Hao OJ (2000) Metal effects on sulfur cycle bacteria and metal removal by sulfate reducing bacteria. In: PNL L, Hulshoff Pol L (eds) Environmental technologies to treat sulfur pollution: principles and engineering. IWA Publishing, London, pp 393–409

Hao T-W, Xiang P-Y, Mackey HR, Chi K, Lu H, Chui H-K, van Loosdrecht MCM, Chen G-H (2014) A review of biological sulfate conversions in wastewater treatment. Water Res 65:1–21. doi:10.1016/j.watres.2014.06.043

Hiibel SR, Pereyra LP, Breazeal MVR, Reisman DJ, Reardon KF, Pruden A (2011) Effect of organic substrate on the microbial community structure in pilot-scale sulfate-reducing biochemical reactors treating mine drainage. Environ Eng Sci 28(8):563–572. doi:10.1089/ees.2010.0237

Huisman JL, Schouten G, Schultz C (2006) Biologically produced sulphide for purification of process streams, effluent treatment and recovery of metals in the metal and mining industry. Hydrometallurgy 83(1–4):106–113. doi:10.1016/j.hydromet.2006.03.017

Hulshoff Pol LW, Lens PNL, Stams AJM, Lettinga G (1998) Anaerobic treatment of sulphate-rich wastewaters. Biodegradation 9(3):213–224. doi:10.1023/A:1008307929134

Hulshoff Pol LW, Lens PNL, Weijma J, Stams AJM (2001) New developments in reactor and process technology for sulfate reduction. Water Sci Technol 44(8):67–76

IWA TGfMMoADP (2002) Anaerobic digestion Model No. 1 (ADM1), IWA.

Johnson DB, Hallberg KB (2005) Biogeochemistry of the compost bioreactor components of a composite acid mine drainage passive remediation system. Sci Total Environ 338(1–2):81–93. doi:10.1016/j.scitotenv.2004.09.008

Jong T, Parry DL (2003) Removal of sulfate and heavy metals by sulfate reducing bacteria in short-term bench scale upflow anaerobic packed bed reactor runs. Water Res 37 (14):3379–3389

Kaksonen AH, Puhakka JA (2007) Sulfate reduction based bioprocesses for the treatment of acid mine drainage and the recovery of metals. Eng Life Sci 7(6):541–564. doi:10.1002/elsc.200720216

Kaksonen AH, Riekkola-Vanhanen ML, Puhakka JA (2003) Optimization of metal sulphide precipitation in fluidized-bed treatment of acidic wastewater. Water Res 37(2):255–266. doi:10.1016/S0043-1354(02)00267-1

Kaksonen AH, Franzmann PD, Puhakka JA (2004) Effects of hydraulic retention time and sulfide toxicity on ethanol and acetate oxidation in sulfate-reducing metal-precipitating fluidized-bed reactor. Biotechnol Bioeng 86(3):332–343. doi:10.1002/bit.20061

Kimura S, Hallberg K, Johnson D (2006) Sulfidogenesis in low pH (3.8–4.2) media by a mixed population of acidophilic bacteria. Biodegradation 17(2):57–65. doi:10.1007/s10532-005-3050-4

König J, Keesman KJ, Veeken A, Lens PNL (2006) Dynamic modelling and process control of ZnS precipitation. Sep Sci Technol 41(6):1025–1042. doi:10.1080/01496390600641546

Koschorreck M, Geller W, Neu T, Kleinsteuber S, Kunze T, Trosiener A, Wendt-Potthoff K (2010) Structure and function of the microbial community in an in situ reactor to treat an acidic mine pit lake. FEMS Microbiol Ecol 73(2):385–395. doi:10.1111/j.1574-6941.2010.00886.x

La H-J, Kim K-H, Quan Z-X, Cho Y-G, Lee S-T (2003) Enhancement of sulfate reduction activity using granular sludge in anaerobic treatment of acid mine drainage. Biotechnol Lett 25(6):503–508. doi:10.1023/A:1022666310393

Labrenz M, Druschel GK, Thomsen-Ebert T, Gilbert B, Welch SA, Kemner KM, Logan GA, Summons RE, Stasio GD, Bond PL, Lai B, Kelly SD, Banfield JF (2000) Formation of sphalerite (ZnS) deposits in natural biofilms of sulfate-reducing bacteria. Science 290 (5497):1744–1747. doi:10.1126/science.290.5497.1744

Lakaniemi A-M, Nevatalo LM, Kaksonen AH, Puhakka JA (2010) Mine wastewater treatment using *Phalaris arundinacea* plant material hydrolyzate as substrate for sulfate-reducing bioreactor. Bioresour Technol 101(11):3931–3939. doi:10.1016/j.biortech.2010.01.020

Larsen PA, Patience DB, Rawlings JB (2006) Industrial crystallization process control. IEEE Ctl Syst Mag 26(4):70–80. doi:10.1109/MCS.2006.1657878

Lauwers J, Appels L, Thompson IP, Degrève J, Impe JFV, Dewil R (2013) Mathematical modelling of anaerobic digestion of biomass and waste: power and limitations. Prog Energy Combust Sci 39(4):383–402. doi:10.1016/j.pecs.2013.03.003

Lefticariu L, Walters ER, Pugh CW, Bender KS (2015). Sulfate reducing bioreactor dependence on organic substrates for remediation of coal-generated acid mine drainage: field experiments. Appl Geochem 63:70–82. doi: 10.1016/j.apgeochem.2015.08.002

Lenz M, van Hullebusch ED, Farges F, Nikitenko S, Corvini PFX, Lens PNL (2011) Combined speciation analysis by X-ray absorption near-edge structure spectroscopy, ion chromatography, and solid-phase microextraction gas chromatography-mass spectrometry to evaluate biotreatment of concentrated selenium wastewaters. Environ Sci Technol 45(3):1067–1073. doi:10.1021/es1022619

Lewis AE (2010) Review of metal sulphide precipitation. Hydrometallurgy 104(2):222–234. doi:10.1016/j.hydromet.2010.06.010

Lewis A, Swartbooi A (2006) Factors affecting metal removal in mixed sulfide precipitation. Chem Eng Technol 29(2):277–280. doi:10.1002/ceat.200500365

Lewis A, van Hille R (2006) An exploration into the sulphide precipitation method and its effect on metal sulphide removal. Hydrometallurgy 81(3–4):197–204. doi:10.1016/j.hydromet.2005.12.009

Liamleam W, Annachhatre AP (2007) Electron donors for biological sulfate reduction. Biotechnol Adv 25(5):452–463. doi:10.1016/j.biotechadv.2007.05.002

Liu W, Zhang J, Jin Y, Zhao X, Cai Z (2015) Adsorption of Pb(II), Cd(II) and Zn(II) by extracellular polymeric substances extracted from aerobic granular sludge: efficiency of protein. J Environ Chem Eng 3(2):1223–1232. doi:10.1016/j.jece.2015.04.009

Lopes SIC, Sulistyawati I, Capela MI, Lens PNL (2007) Low pH (6, 5 and 4) sulfate reduction during the acidification of sucrose under thermophilic (55°C) conditions. Process Biochem 42 (4):580–591. doi:10.1016/j.procbio.2006.11.004

Luptakova A, Kusnierova M (2005) Bioremediation of acid mine drainage contaminated by SRB. Hydrometallurgy 77(1–2):97–102. doi:10.1016/j.hydromet.2004.10.019

Mersmann A (1999) Crystallization and precipitation. Chem Eng Process 38(4–6):345–353. doi:10.1016/S0255-2701(99)00025-2

Mes TZDD, Stams AJM, Reith JH, Zeeman G (2003) Methane production by anaerobic digestion of wastewater and solid wastes. In: Reith JH, Wijffels RH, Barten H (eds) Bio-methane & bio-hydrogen: status and perspectives of biological methane and hydrogen production. The Hague, Dutch Biological Hydrogen Foundation – NOVEM, pp 58–102

Meulepas RJW, Stams AM, Lens PL (2010) Biotechnological aspects of sulfate reduction with methane as electron donor. Rev Environ Sci Biotechnol 9(1):59–78. doi:10.1007/s11157-010-9193-8

Mishra PK, Das RP (1992) Kinetics of zinc and cobalt sulphide precipitation and its application in hydrometallurgical separation. Hydrometallurgy 28(3):373–379. doi:10.1016/0304-386X(92)90042-X

Mizuno O, Li YY, Noike T (1998) The behavior of sulfate-reducing bacteria in acidogenic phase of anaerobic digestion. Water Res 32(5):1626–1634. doi:10.1016/s0043-1354(97)00372-2

Mokone TP, van Hille RP, Lewis AE (2010) Effect of solution chemistry on particle characteristics during metal sulfide precipitation. J Colloid Interface Sci 351(1):10–18. doi:10.1016/j.jcis.2010.06.027

Moosa S, Harrison STL (2006) Product inhibition by sulphide species on biological sulphate reduction for the treatment of acid mine drainage. Hydrometallurgy 83(1–4):214–222. doi:10.1016/j.hydromet.2006.03.026

Muyzer G, Stams AJM (2008) The ecology and biotechnology of sulphate-reducing bacteria. Nat Rev Micro 6(6):441–454. doi:10.1038/nrmicro1892

Nagpal S, Chuichulcherm S, Peeva L, Livingston A (2000) Microbial sulfate reduction in a liquid-solid fluidized bed reactor. Biotechnol Bioeng 70(4):370–380. doi:10.1002/1097-0290(20001120)70:4<370::aid-bit2>3.0.co;2-7

Ňancucheo I, Johnson DB (2012) Selective removal of transition metals from acidic mine waters by novel consortia of acidophilic sulfidogenic bacteria. Microb Biotechnol 5(1):34–44. doi:10.1111/j.1751-7915.2011.00285.x

Ňancucheo I, Johnson DB (2014) Removal of sulfate from extremely acidic mine waters using low pH sulfidogenic bioreactors. Hydrometallurgy 150:222–226. doi:10.1016/j.hydromet.2014.04.025

Neculita C-M, Zagury GJ, Bussiere B (2007) Passive treatment of acid mine drainage in bioreactors using sulfate-reducing bacteria: critical review and research needs. J Environ Qual 36 (1):1–16. doi:10.2134/jeq2006.0066

Neculita C-M, Zagury GJ, Bussière B (2008) Effectiveness of sulfate-reducing passive bioreactors for treating highly contaminated acid mine drainage: II. Metal removal mechanisms and potential mobility. Appl Geochem 23(12):3545–3560. doi:10.1016/j.apgeochem.2008.08.014

Nguyen D, Gadhamshetty V, Nitayavardhana S, Khanal SK (2015) Automatic process control in anaerobic digestion technology: a critical review. Bioresour Technol 193:513–522. doi:10.1016/j.biortech.2015.06.080

Papirio S, Villa-Gómez DK, Esposito G, Pirozzi F, Lens PNL (2012) Acid mine drainage treatment in fluidized-bed bioreactors by sulfate-reducing bacteria: a critical review. Crit Rev Environ Sci Technol 43(23):2545–2580. doi:10.1080/10643389.2012.694328

Paques BV (2016) Paques, leading in biological wastewater and gas treatment [Online]. Available: www.paques.nl. Accessed 10 Jan 2016

Parker WJ, Wu GH (2006) Modifying ADM1 to include formation and emission of odourants. Water Sci Technol 54(4):111–117. doi:10.2166/wst.2006.532

Parshina SN, Kijlstra S, Henstra AM, Sipma J, Plugge CM, Stams AJM (2005a) Carbon monoxide conversion by thermophilic sulfate-reducing bacteria in pure culture and in co-culture with *Carboxydothermus hydrogenoformans*. Appl Microbiol Biotechnol 68(3):390–396

Parshina SN, Sipma J, Nakashimada Y, Henstra AM, Smidt H, Lysenko AM, Lens PNL, Lettinga G, Stams AJM (2005b) *Desulfotomaculum carboxydivorans* sp. nov., a novel sulfate-reducing bacterium capable of growth at 100% CO. Int J Syst Evol Microbiol 55 (5):2159–2165. doi:10.1099/ijs.0.63780-0

Parshina SN, Sipma J, Henstra AM, Stams AJM (2010) Carbon monoxide as an electron donor for the biological reduction of sulphate Int J Microbiol 2010:9. doi: 10.1155/2010/319527

Pat-Espadas AM, Field JA, Otero-Gonzalez L, Razo-Flores E, Cervantes FJ, Sierra-Alvarez R (2016) Recovery of palladium(II) by methanogenic granular sludge. Chemosphere 144:745–753. doi:10.1016/j.chemosphere.2015.09.035

Pind P, Angelidaki I, Ahring B, Stamatelatou K, Lyberatos G (2003) Monitoring and control of anaerobic reactors. In: Biomethanation II, vol 82, Series on Advances in Biochemical Engineering/biotechnology. Springer, Berlin/Heidelberg, pp 135–182. doi:10.1007/3-540-45838-7_4

Pokhrel LR, Dubey B (2013) Global scenarios of metal mining, environmental repercussions, public policies, and sustainability: a review. Crit Rev Environ Sci Technol 43(21):2352–2388. doi:10.1080/10643389.2012.672086

Prange A, Modrow H (2002) X-ray absorption spectroscopy and its application in biological, agricultural and environmental research. Rev Environ Sci Biotechnol 1(4):259–276. doi:10.1023/a:1023281303220

Puigdomènech I (2010) Make equilibrium diagrams using sophisticated algorithms (MEDUSA), software version 18 February 2004. Inorganic Chemistry Department, Royal Institute of Technology, Stockholm

Qinglin X, Yanhong L, Shaoyuan B, Hongda J (2012) Effects of ORP, recycling rate, and HRT on simultaneous sulfate reduction and sulfur production in expanded granular sludge bed (EGSB) reactors under micro-aerobic conditions for treating molasses distillery wastewater. Water Sci Technol 66(6):1253–1262. doi:10.2166/wst.2012.311

Reis MAM, Almeida JS, Lemos PC, Carrondo MJT (1992) Effect of hydrogen sulfide on growth of sulfate reducing bacteria. Biotechnol Bioeng 40(5):593–600. doi:10.1002/bit.260400506

Rittmann BE, McCarty PL (2001) Environmental biotechnology: principles and applications. McGraw-Hill, New Delhi

Roland H, Benjamin S (2015) Mining & metals in a sustainable world 2050. Switzerland

Sahinkaya E, Gungor M (2010) Comparison of sulfidogenic up-flow and down-flow fluidized-bed reactors for the biotreatment of acidic metal-containing wastewater. Bioresour Technol 101 (24):9508–9514. doi:10.1016/j.biortech.2010.07.113

Sahinkaya E, Yucesoy Z (2010) Biotreatment of acidic zinc- and copper-containing wastewater using ethanol-fed sulfidogenic anaerobic baffled reactor. Bioprocess Biosyst Eng 33 (8):989–997. doi:10.1007/s00449-010-0423-9

Sahinkaya E, Gungor M, Bayrakdar A, Yucesoy Z, Uyanik S (2009) Separate recovery of copper and zinc from acid mine drainage using biogenic sulfide. J Hazard Mater 171(1–3):901–906. doi:10.1016/j.jhazmat.2009.06.089

Sahinkaya E, Gunes FM, Ucar D, Kaksonen AH (2011) Sulfidogenic fluidized bed treatment of real acid mine drainage water. Bioresour Technol 102(2):683–689. doi:10.1016/j.biortech.2010.08.042

Samaranayake R, Singhal N, Lewis G, Hyland M (2002) Kinetics of biochemically driven metal precipitation in synthetic landfill leachate. Remed J 13(1):137–150. doi:10.1002/rem.10060

Sampaio RMM, Timmers RA, Xu Y, Keesman KJ, Lens PNL (2009) Selective precipitation of Cu from Zn in a pS controlled continuously stirred tank reactor. J Hazard Mater 165 (1–3):256–265. doi:10.1016/j.jhazmat.2008.09.117

Sampaio RMM, Timmers RA, Kocks N, André V, Duarte MT, van Hullebusch ED, Farges F, Lens PNL (2010) Zn-Ni sulfide selective precipitation: the role of supersaturation. Sep Purif Technol 74(1):108–118. doi:10.1016/j.seppur.2010.05.013

Sanchez-Andrea I, Triana D, Sanz JL (2012) Bioremediation of acid mine drainage coupled with domestic wastewater treatment. Water Sci Technol 66(11):2425–2431. doi:10.2166/wst.2012.477

Sánchez-Andrea I, Sanz JL, Bijmans MFM, Stams AJM (2014) Sulfate reduction at low pH to remediate acid mine drainage. J Hazard Mater 269:98–109. doi:10.1016/j.jhazmat.2013.12.032

Shakeri Yekta S, Gustavsson J, Svensson BH, Skyllberg U (2012) Sulfur K-edge XANES and acid volatile sulfide analyses of changes in chemical speciation of S and Fe during sequential extraction of trace metals in anoxic sludge from biogas reactors. Talanta 89:470–477. doi:10.1016/j.talanta.2011.12.065

Sierra-Alvarez R, Karri S, Freeman S, Field JA (2006) Biological treatment of heavy metals in acid mine drainage using sulfate reducing bioreactors. Water Sci Technol 54(2):179–185

Sipma J, Henstra AM, Parshina SN, Lens PNL, Lettinga G, Stams AJM (2006) Microbial CO conversions with applications in synthesis gas purification and bio-desulfurization. Crit Rev Biotechnol 26(1):41–65. doi:10.1080/07388550500513974

Sipma J, Begoña Osuna M, Lettinga G, Stams AJM, Lens PNL (2007) Effect of hydraulic retention time on sulfate reduction in a carbon monoxide fed thermophilic gas lift reactor. Water Res 41(9):1995–2003. doi:10.1016/j.watres.2007.01.030

Song H, Yim G, Ji S, Nam I, Neculita C, Lee G (2012) Performance of mixed organic substrates during treatment of acidic and moderate mine drainage in column bioreactors. J Environ Eng 138(10):1077–1084. doi:10.1061/(ASCE)EE.1943-7870.0000567

Sousa JAB, Plugge CM, Stams AJM, Bijmans MFM (2015) Sulfate reduction in a hydrogen fed bioreactor operated at haloalkaline conditions. Water Res 68:67–76. doi:10.1016/j.watres.2014.09.035

Tabak HH, Govind R (2003) Advances in biotreatment of acid mine drainage and biorecovery of metals: 2. Membrane bioreactor system for sulfate reduction. Biodegradation 14(6):437–452. doi:10.1023/A:1027332918844

Tabak HH, Scharp R, Burckle J, Kawahara FK, Govind R (2003) Advances in biotreatment of acid mine drainage and biorecovery of metals: 1. Metal precipitation for recovery and recycle. Biodegradation 14(6):423–436. doi:10.1023/A:1027332902740

Tang Y, Ontiveros-Valencia A, Feng L, Zhou C, Krajmalnik-Brown R, Rittmann BE (2013) A biofilm model to understand the onset of sulfate reduction in denitrifying membrane biofilm reactors. Biotechnol Bioeng 110(3):763–772. doi:10.1002/bit.24755

Tokuda H, Kuchar D, Mihara N, Kubota M, Matsuda H, Fukuta T (2008) Study on reaction kinetics and selective precipitation of Cu, Zn, Ni and Sn with H_2S in single-metal and multi-metal systems. Chemosphere 73(9):1448–1452. doi:10.1016/j.chemosphere.2008.07.073

Torner-Morales FJ, Buitrón G (2010) The redox potential as the limiting factor to carry out a combined sulfate-reducing/sulfide-oxidizing process in a single SBR. In: Proceedings of the 12th world congress on anaerobic digestion, Guadalajara, Mexico, 31 October–4 November

Utgikar VP, Harmon SM, Chaudhary N, Tabak HH, Govind R, Haines JR (2002) Inhibition of sulfate-reducing bacteria by metal sulfide formation in bioremediation of acid mine drainage. Environ Toxicol 17(1):40–48. doi:10.1002/tox.10031/abstract

Utgikar VP, Chaudhary N, Koeniger A, Tabak HH, Haines JR, Govind R (2004) Toxicity of metals and metal mixtures: analysis of concentration and time dependence for zinc and copper. Water Res 38(17):3651–3658. doi:10.1016/j.watres.2004.05.022

Vakili M, Gholami Z, Gholami F (2012) Removal of hydrogen sulfide from gaseous streams by a chemical method using ferric sulfate solution. World Appl Sci J 19(2):241–245. doi:10.5829/idosi.wasj.2012.19.02.1541

van Hille RP, Peterson KA, Lewis AE (2005) Copper sulphide precipitation in a fluidised bed reactor. Chem Eng Sci 60(10):2571–2578. doi:10.1016/j.ces.2004.11.052

van Hullebusch E, Zandvoort M, Lens P (2003) Metal immobilisation by biofilms: mechanisms and analytical tools. Rev Environ Sci Biotechnol 2(1):9–33. doi:10.1023/B:RESB.0000022995.48330.55

van Hullebusch ED, Zandvoort MH, Lens PNL (2004) Nickel and cobalt sorption on anaerobic granular sludges: kinetic and equilibrium studies. J Chem Technol Biotechnol 79(11):1219–1227. doi:10.1002/jctb.1116

van Hullebusch ED, Peerbolte A, Zandvoort MH, Lens PNL (2005) Sorption of cobalt and nickel on anaerobic granular sludges: isotherms and sequential extraction. Chemosphere 58(4):493–505. doi:10.1016/j.chemosphere.2004.09.017

van Hullebusch ED, Gieteling J, Zhang M, Zandvoort MH, Daele WV, Defrancq J, Lens PNL (2006) Cobalt sorption onto anaerobic granular sludge: isotherm and spatial localization analysis. J Biotechnol 121(2):227–240. doi:10.1016/j.jbiotec.2005.07.011

van Hullebusch ED, Rossano S, Farges F, Lenz M, Labanowski J, Lagarde P, Flank AM, Lens PNL (2009) Sulfur K-edge XANES spectroscopy as a tool for understanding sulfur chemical state in anaerobic granular sludge. J Phys Conf Ser 190:012184. doi:10.1088/1742-6596/190/1/012184

Vanwonterghem I, Jensen PD, Ho DP, Batstone DJ, Tyson GW (2014) Linking microbial community structure, interactions and function in anaerobic digesters using new molecular techniques. Curr Opin Biotechnol 27:55–64. doi:10.1016/j.copbio.2013.11.004

Veeken AHM, Akoto L, Hulshoff Pol LW, Weijma J (2003a) Control of the sulfide (S) concentration for optimal zinc removal by sulfide precipitation in a continuously stirred tank reactor. Water Res 37(15):3709–3717. doi:10.1016/S0043-1354(03)00262-8

Veeken AHM, de Vries S, van der Mark A, Rulkens WH (2003b) Selective precipitation of heavy metals as controlled by a sulfide-selective electrode. Sep Sci Technol 38(1):1–19. doi:10.1081/SS-120016695

Villa-Gómez DK, Enright AM, Rini EL, Buttice A, Kramer H, Lens P (2015) Effect of hydraulic retention time on metal precipitation in sulfate reducing inverse fluidized bed reactors. J Chem Technol Biotechnol 90(1):120–129. doi:10.1002/jctb.4296

Villa-Gómez D, Ababneh H, Papirio S, Rousseau DPL, Lens PNL (2011) Effect of sulfide concentration on the location of the metal precipitates in inversed fluidized bed reactors. J Hazard Mater 192(1):200–207. doi:10.1016/j.jhazmat.2011.05.002

Villa-Gómez DK, Papirio S, van Hullebusch ED, Farges F, Nikitenko S, Kramer H, Lens PNL (2012) Influence of sulfide concentration and macronutrients on the characteristics of metal precipitates relevant to metal recovery in bioreactors. Bioresour Technol 110(0):26–34. doi:10.1016/j.biortech.2012.01.041

Villa-Gómez DK, Cassidy J, Keesman KJ, Sampaio R, Lens PNL (2014a) Sulfide response analysis for sulfide control using a pS electrode in sulfate reducing bioreactors. Water Res 50(0):48–58. doi:10.1016/j.watres.2013.10.006

Villa-Gómez DK, van Hullebusch ED, Maestro R, Farges F, Nikitenko S, Kramer H, Gonzalez-Gil G, Lens PNL (2014b) Morphology, mineralogy, and solid-liquid phase separation characteristics of Cu and Zn precipitates produced with biogenic sulfide. Environ Sci Technol 48(1):664–673. doi:10.1021/es402795x

Wakeman KD, Erving L, Riekkola-Vanhanen ML, Puhakka JA (2010) Silage supports sulfate reduction in the treatment of metals- and sulfate-containing waste waters. Water Res 44(17):4932–4939. doi:10.1016/j.watres.2010.07.025

Willow MA, Cohen RRH (2003) pH, dissolved oxygen, and adsorption effects on metal removal in anaerobic bioreactors. J Environ Qual 32(4):1212–1221. doi:10.2134/jeq2003.1212

Zhang Y, Henriet JP, Bursens J, Boon N (2010) Stimulation of in vitro anaerobic oxidation of methane rate in a continuous high-pressure bioreactor. Bioresour Technol 101(9):3132–3138. doi:10.1016/j.biortech.2009.11.103

Zhou J, Xing J (2015) Effect of electron donors on the performance of haloalkaliphilic sulfate-reducing bioreactors for flue gas treatment and microbial degradation patterns related to sulfate reduction of different electron donors. Biochem Eng J 96:14–22. doi:10.1016/j.bej.2014.12.015

Zhou J, Zhou X, Li Y, Xing J (2015) Bacterial communities in haloalkaliphilic sulfate-reducing bioreactors under different electron donors revealed by 16S rRNA MiSeq sequencing. J Hazard Mater 295:176–184. doi:10.1016/j.jhazmat.2015.04.010

Chapter 4
Biological Sulphate Reduction

Pimluck Kijjanapanich and Piet N.L. Lens

Abstract During construction, renovation and/or demolition activities, large amounts of construction and demolition debris are created. This debris contains high sulphate concentrations and toxic metals, which can create a lot of environmental problems, especially at landfill sites. The disposal of the debris can cause odour problems and possible health impacts to landfill staff and surrounding inhabitants due to hydrogen sulphide gas generation. In order to reuse this debris, sulphate and heavy metal have to be removed. This chapter reviews the technologies used for sulphate and heavy metal removal from the debris both by chemical and biological processes. Moreover, possible ways for sulphur recovery has been reviewed. A sulphate removal efficiency up to 99% can be achieved from the chemical sulphate removal process. However, for this high performance, toxic chemicals such as barium and lead compounds have to be used. The biological sulphate reduction process is an alternative method for sulphate removal and recovery of sulphur and heavy metals from debris. Sulphide which is the product of this bio-process can be easily precipitated together with dissolved metal as metallic sulphides. Moreover, sulphide produced in this process can also be recovered as elemental sulphur or sulphuric acid.

Keywords Construction and demolition debris • Gypsum contaminated waste • Sulphate reducing bacteria • Sulphate reduction

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P. Kijjanapanich (✉)
UNESCO-IHE Institute for Water Education, Delft, The Netherlands

Department of Environmental Engineering, Faculty of Engineering, Chiang Mai University, Chiang Mai 50200, Thailand
e-mail: pimluck@eng.cmu.ac.th

P.N.L. Lens
UNESCO-IHE Institute for Water Education, Delft, The Netherlands

Department of Chemistry and Bioengineering, Tampere University of Technology, PO Box 10541, Tampere, Finland
e-mail: p.lens@un-ihe.org

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Contents

4.1 Introduction

Solid wastes containing sulphate, such as construction and demolition debris, phosphogypsum and flue gas desulphurisation gypsum, are an important source of pollution, which can create a lot of environmental problems (Kaufman et al. 1996; Azabou et al. 2007; Delaware Solid Waste Authority 2008; U.S.EPA. 2008; Kijjanapanich et al. 2013, 2014c). Nowadays, large quantities of these wastes are generated due to industrial growth. Table 4.1 shows the generated amounts of sulphate contaminated solid wastes and the possible toxic compounds contained in it.

Construction, renovation or demolition activities yield large amounts of wastes. With insufficient source separation, debris becomes a mixed material which is difficult to recycle (Montero et al. 2010). This debris usually contains small pieces of gypsum drywall, wood, paper, rock, concrete, plastic and metals (Table 4.2). Debris has been associated with odour problems at many landfills (Jang 2000). This because debris can contribute to the growth of anaerobic bacteria under wet conditions when it is disposed together with organic waste (Gypsum Association 1992a). Therefore, it is suggested that debris should be placed separate from other wastes, especially organic waste, in a specific area of the landfill. This results in the rapid rise of the disposal costs of debris (Gypsum Association 1992b). Nearly 40% of the total debris mass consists of the fine fraction, called sand debris, which contains high amounts of sulphate (in form of gypsum) (Montero et al. 2010). The content of gypsum (by mass) in sand debris ranges from 1.5 to 16.0% (Jang and Townsend 2001a; Kijjanapanich et al. 2013). Montero et al. (2010) found that organic matter was distributed mainly in fractions composed of large-sized components, whereas the gypsum was concentrated in the fine fraction (52.4%). In order to reduce the amount of debris going to a specific area of the landfill, the sand debris has to be separated from the mixed debris. However, final disposal or reuse still requires removing of sulphate from the sand debris.

Although debris can be reused as building materials or soil amendment, a concern has been raised by regulators regarding the chemical composition of the solid waste materials and the potential risks to human health and the environment, due to elevated concentrations of sulphate, polycyclic aromatic hydrocarbons and

Table 4.1 Amount of sulphate contaminated solid wastes generated and their possibly toxic contaminants

Type of solid waste	The amount generation	Toxic compounds	References
Construction and demolition debris	4.9 kg per m^2 of the structure	Heavy metal such as aluminium, arsenic, cadmium, chromium, copper, zinc, lead and barium and organic compounds, such as toluene, trichlorofluoromethane and several polycyclic aromatic hydrocarbons	Jang and Townsend (2001a, b), Kijjanapanich et al. (2013) and Turley (1998)
Phosphogypsum	5 tons per ton of phosphorus pentoxide production or 100–280 million tons per year worldwide	Residual acid, fluoride, toxic metals such as lead, selenium, strontium and cerium, and radioactive compounds such as uranium, radium and radon	Tayibi et al. (2009), Mulopo and Ikhu-Omoregbe (2012), Azabou et al. (2005) and Rutherford et al. (1995)
Flue gas desulphurisation gypsum	–	Fluoride, toxic metals such as mercury and selenium	Shaw (2008)

Table 4.2 Typical components of construction and demolition debris generated by new residential construction

Components	Content examples	Percent (%)
Wood	Forming and framing lumber, stumps/trees, engineered wood, plywood, laminates, scraps	8.0–42.4
Drywall	Sheetrock, gypsum, plaster	4.4–27.3
Concrete and asphalt pavement	Foundations, driveways, sidewalks, floors, road surface, sidewalks and road structures made with asphalt binder	12.0–56.2
Brick	Bricks and decorative blocks	7.3
Metals	Pipes, rebar, flashing, steel, aluminium, copper, brass, stainless steel, wiring, framing	1.8
Plastics	Vinyl siding, doors, windows, floor tile, pipes, packaging	0.7–1.4
Roofing	Asphalt & wood shingles, slate, tile, roofing felt	1.4
Glass	Windows, mirrors, lights	1.8
Miscellaneous	Carpeting, fixtures, insulation, ceramic tile	0.6–14.6
Cardboard	From newly installed items such as appliances and tile	5.4

U.S.EPA. (1998); Jang and Townsend (2001a); U.S.EPA. (2003); California Contra Costa County (2013) and Kijjanapanich et al. (2013)

heavy metals contained in the debris (Table 4.3) (Jang and Townsend 2001a; Jang and Townsend 2001b; Kijjanapanich et al. 2013). Jang and Townsend (2001b) analysed volatile and semi-volatile organic compounds present in debris from 14 debris recycling facilities in south Florida. They found that toluene showed the highest leachability among the compounds (61.3–92.0%), while trichlorofluoromethane, the most commonly detected compound in debris, had the lowest leachability (1.4–39.9%). Several polycyclic aromatic hydrocarbons also leached during the leaching tests from debris (Jang and Townsend 2001b). The results from their study indicate that, under reuse scenarios, the organics in debris recycling facilities were not a major concern, especially from the view-point of human health risk and leaching risk to groundwater (Jang and Townsend 2001b).

In order to reuse sand debris as sand for constructions, the sulphate content in sand has to be considered. If sand is present in a high sulphate content, it can cause negative effects on the properties of the produced concrete such as softening effect, strength loss and cracking of the concrete. For example, the Dutch government has set limits to the maximum amount of polluting compounds present in building material. For reusable sand, the maximum allowable concentration is set to 1.73 g sulphate per kg of sand (de Vries 2006). However, most of the sand debris still remains highly polluted, and the sulphate content often exceeds the prescribed limit (de Vries 2006; Kijjanapanich et al. 2013).

A biological sulphate reduction treatment is an attractive alternative for sulphate removal for this kind of solid wastes. In the past, biological sulphate reduction has been considered as unwanted in anaerobic wastewater treatment (Hulshoff Pol et al. 1998). In contrast, nowadays interest has grown in applying biological sulphate

Table 4.3 Characteristics of sand debris leachate (Solid: Liquid ratio = 1:10)

Parameter		Sand debris
pH		7.71 ± 0.07
Macro nutrients (mg L^{-1})	Sulphate	1760.24 ± 30.44
	Na	40.85 ± 0.67
	Mg	21.86 ± 1.51
	K	27.58 ± 0.59
	Ca	589.33 ± 8.33
Heavy metals (μg L^{-1})	Al	57.64 ± 17.18
	Cr	<2
	Mn	199.93 ± 6.31
	Fe	81.41 ± 15.93
	Co	5.60 ± 0.15
	Ni	11.32 ± 0.37
	Cu	30.68 ± 1.65
	Zn	67.58 ± 2.38
	As	5.22 ± 0.08
	Mo	26.54 ± 2.21
	Cd	<2
	Ba	71.80 ± 0.90
	Pb	6.12 ± 1.53

Kijjanapanich et al. (2013)

reduction for the treatment of specific waste streams (inorganic sulphate rich wastewaters), such as acid mine drainage or wastewater containing sulphuric acid (H_2SO_4) (Sahinkaya et al. 2011a; Kijjanapanich et al. 2012), which is often coupled to heavy metal removal (Jong and Parry 2003; Liamleam 2007; Kijjanapanich et al. 2012). However, research on biological sulphate reduction has mainly focused on the treatment of sulphate containing groundwater or wastewaters, while research on bioremediation of debris especially using sulphate reducing bacteria is rare.

4.2 Chemical Versus Biological Treatment for Sulphate and Heavy Metal Removal

Table 4.4 summarises the advantages and disadvantages of the chemical sulphate removal and the biological sulphate reduction processes.

4.2.1 *Chemical Treatment*

Debris can be treated in different ways depending on the application. Most simple treatments of these wastes are chemical or physical treatment such as washing, wet sieving, or neutralisation with lime (Tayibi et al. 2009). Some of these wastes can be treated by thermal treatment to produce anhydrite for construction and cement industry applications (Singh and Garg 2000; Taher 2007).

Table 4.4 Advantages and disadvantages of the chemical sulphate removal and the biological sulphate reduction processes

Treatment type	Advantages	Disadvantages
Chemical sulphate removal	High sulphate removal efficiency	Expensive chemicals
	Require short treatment times	Remaining of toxic chemical in the treated water
	Require small reactor volume	Require liquid-solid separation system
	No need for a sophisticated operation	
	Low maintenance costs (requiring only replenishment of the chemicals used)	
Biological sulphate reduction	Both sulphate and metals can be reduced to very low levels	Slow process kinetics
	The amount of waste produced is minimal	Requirement and cost of an external electron donor
	Capital costs are relatively low	Need for a post-treatment of the sulphide containing effluent
	Operating costs can be drastically reduced by using no or low cost electron donor and carbon sources	
	Less toxic compounds produced	

At landfill sites, the utilisation of specific cover material to control hydrogen sulphide (H_2S) emissions can be a useful alternative technique which is cheaper than landfill gas collection systems. Lime and fine concrete amended soil demonstrated the best performance in reducing hydrogen sulphide emissions compared to clayey and sandy soils (Plaza et al. 2007). Plaza et al. (2007) also concluded that the particle size of the cover material is important, as the amount of sorption will increase with an increase in available surface area. However, this kind of treatment is an end-of-pipe solution, which may be insufficient to confine the adverse effects of stored debris.

Sulphate and heavy metal removal processes can be either by biological or chemical processes (Azabou et al. 2007; Dar et al. 2007; Hlabela et al. 2007; Benatti et al. 2009). A variety of physico-chemical treatment processes are employed for sulphate and heavy metal removal such as ion exchange, adsorption and membrane filtration. These technologies are, however, relatively expensive due to their higher operation and maintenance costs as well as energy consumption (Ozacar et al. 2008). Chemical precipitation is a well-established technology with ready availability of equipment and chemicals (U.S.EPA. 2000). Barium and lead compounds, such as barium chloride ($BaCl_2$) and lead nitrate ($Pb(NO_3)_2$), are well-known efficient chemicals for sulphate removal (Eqs. 4.1 and 4.2) (Maree et al. 2004; Benatti et al. 2009) with a sulphate removal efficiency up to 90–99% (Bosman et al. 1990; Hlabela et al. 2007; Kijjanapanich et al. 2014a).

$$Ba^{2+}{}_{(aq)} + SO_4^{2-}(aq) \rightarrow BaSO_{4(s)} \tag{4.1}$$

$$Pb^{2+}{}_{(aq)} + SO_4^{2-}(aq) \rightarrow PbSO_{4(s)} \tag{4.2}$$

$$Ca^{2+}{}_{(aq)} + SO_4^{2-}(aq) \rightarrow CaSO_{4(s)} \tag{4.3}$$

Although barium and lead compounds show good performance in sulphate precipitation, residual barium and lead which remains in the treated leachate or material after the precipitation process are toxic (Benatti et al. 2009). They can result in an adverse impact on the environment if these are discharged or used without post-treatment. The study of Nadagouda et al. (2011) reports a synthesis of barium carbonate ($BaCO_3$) loaded polyvinyl chloride composites which can be used for sulphate removal. With this technique the solubility issues of barium in treated water can be eliminated, thus reducing waste of barium carbonate and environmental issues.

Calcium compounds, such as calcium chloride ($CaCl_2$) and calcium oxide (CaO), can be cheap alternative chemicals for sulphate removal (Eq. 4.3) (Bosman et al. 1990; Maree et al. 2004; Hlabela et al. 2007; Benatti et al. 2009), as these are less toxic than barium and lead. However, if calcium was used as precipitant, a residual sulphate concentration of up to 1450 mg L^{-1} of sulphate will remain due to the high solubility of calcium sulphate (gypsum). In addition, systems for precipitate separation and appropriate reuse or disposal of the solid phase are necessary when using chemical sulphate removal processes (Silva et al. 2002).

Remediation techniques for heavy metal removal such as physico-chemical treatment by pH adjustment to the alkaline range followed by metal hydroxide precipitation have been employed (Morrison and Spangler 1992, 1993; Ngwenya et al. 2006; Huttagosol and Kijjanapanich 2008). However, these methods are expensive and produce large volumes of inorganic sludge which are often difficult to dispose of due to their toxicity (Elliott et al. 1998).

4.2.2 Biological Treatment

A novel approach for the removal of sulphate based on the biological treatment of sulphate containing wastewater (Waybrant et al. 1998; Benner et al. 1999; Annachhatre and Suktrakoolvait 2001; Costa et al. 2007) has been proposed and has also been applied for the treatment of debris leachate (Kijjanapanich et al. 2013, 2014d). This approach uses the bacterial sulphate reduction process as it occurs in nature (Jong and Parry 2003; Liamleam 2007; Kijjanapanich et al. 2012, 2014c). The biological sulphate reduction approach involves the use of anaerobic sulphate reducing bacteria, which reduce sulphate to sulphide by oxidising an organic carbon source (Eq. 4.4):

$$2CH_2O + SO_4^{2-} + 2H^+ \rightarrow H_2S + 2CO_2 + 2H_2O \tag{4.4}$$

where CH_2O represents a simple organic compound. The addition of an electron donor, such as ethanol or lactate is necessary in case of biological sulphate reduction (Liamleam and Annachhatre 2007; Kijjanapanich et al. 2013, 2014d). However, low or no cost organic substrates, such as wood chips, compost, and sewage sludge, can also be used (Waybrant et al. 1998; Gibert et al. 2004; Kijjanapanich et al. 2012, 2014b). These organic substrates are much cheaper and less toxic compared to bulk chemicals (Table 4.4).

The biogenic sulphide (Eq. 4.4) easily precipitates many of the dissolved metal ions as low solubility metallic sulphides (Gibert et al. 2004) (Eq. 4.5):

$$H_2S + M^{2+} \rightarrow MS_{(S)} + 2H^+ \tag{4.5}$$

where M represents metals such as iron, zinc, nickel, copper, and lead. In addition, sulphide precipitation of metals has several benefits over the hydroxide precipitation, including lower solubility, better thickening characteristics of the metal sludge and the possibility to recover valuable metal (Whang et al. 1982; Veeken and Rulkens 2003; Kaksonen and Puhakka 2007).

Many types of bioreactors have been used for the sulphate reduction step (Annachhatre and Suktrakoolvait 2001; Vallero et al. 2005; Nevatalo et al. 2010; Sahinkaya et al. 2011a; Villa-Gomez et al. 2011; Kijjanapanich et al. 2013, 2014d). For example, the Upflow Anaerobic Sludge Blanket (UASB) Reactor (Fig. 4.1a) which biomass retention is based on good settling characteristics of granular sludge (Lettinga et al. 1980) and is the most widely used reactor type for anaerobic wastewater treatment, Inverse Fluidised Bed (IFB) Reactor (Fig. 4.1b) which is

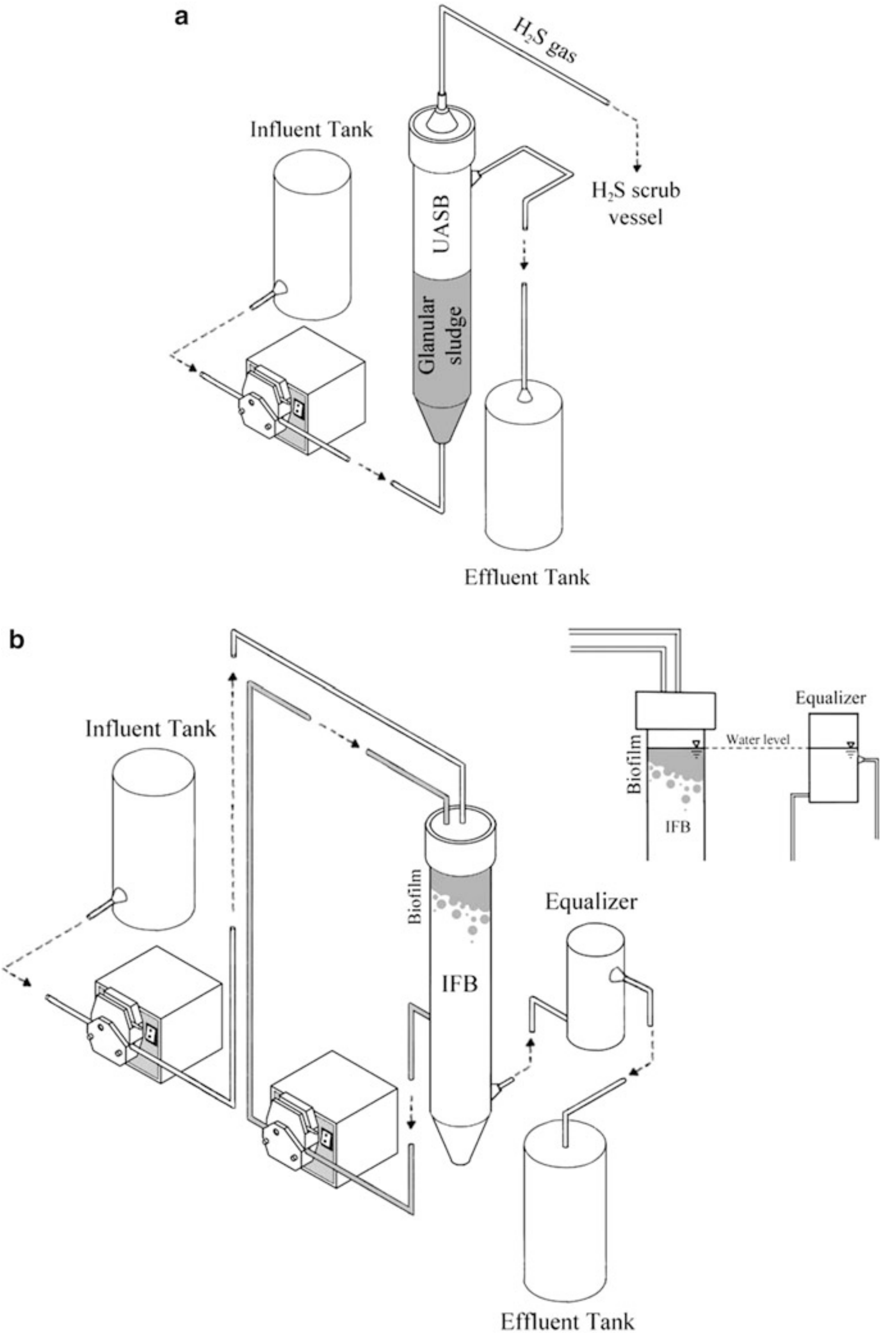

Fig. 4.1 Schematic diagram of sulphate reducing bioreactors: (**a**) Upflow Anaerobic Sludge Blanket (UASB) Reactor, (**b**) Inverse Fluidised Bed (IFB) Reactor and (**c**) Gas Lift Anaerobic Membrane Bioreactor. Sulphate reduction in these bioreactor configurations is compared in Kijjanapanich et al. (2014d)

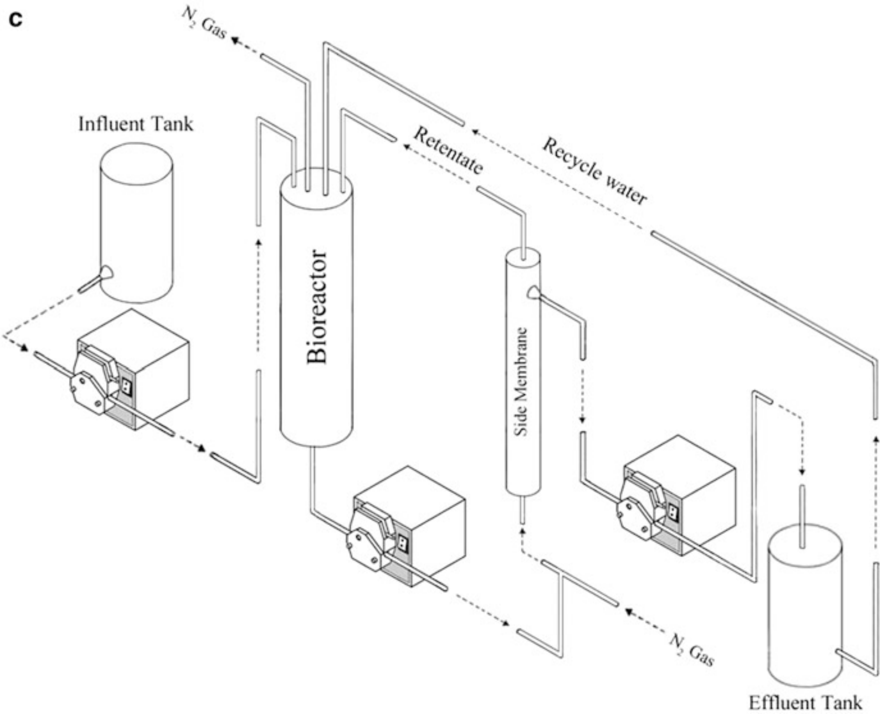

Fig. 4.1 (continued)

based on floatable carrier material which is fluidised downward with a downflow current of liquid, results a promising reactor configuration for combined biological sulphate reduction (upper part of the reactor) and metal precipitate (bottom of the reactor) separation in a single unit (Villa-Gomez et al. 2011) and Anaerobic Membrane Bioreactor which is suitable for slow growing microorganisms, has a smaller reactor footprint and produces excellent effluent quality (Lee and Kim 2009) (Fig. 4.1c).

4.3 Biological Sulphate Removal for Construction and Demolition Debris Treatment

4.3.1 Direct Versus Indirect Treatment

Gypsum contaminated solid wastes, such as construction and demolition debris, phosphogypsum and flue gas desulphurisation gypsum can be treated by biological sulphate reduction (Wolicka and Borkowski 2009; Zhao et al. 2010; Castillo et al. 2012; Kijjanapanich et al. 2013). Sulphate contained in these solid wastes was shown to be a good source of sulphate for sulphate reducing bacteria in several studies (Rzeczycka et al. 2004; Wolicka and Kowalski 2006; Kijjanapanich et al. 2013). Treatment of these solid wastes can be done in two ways (Fig. 4.2): an indirect (Fig. 4.3a) or a direct (Fig. 4.3b) treatment. In the indirect treatment concept, debris is washed to remove most of the impurities and to obtain the right physical characteristics (de Vries 2006; Kijjanapanich et al. 2013, 2014c). The gypsum contained in the debris is thus leached out by water in this leaching step. The sulphate containing leachate is then further treated in a biological sulphate reduction step. The treated water from the bioreactor can then be reused in the leaching column (Fig. 4.3a). The leaching step was found to be the most time consuming step for this kind of treatment (Kijjanapanich et al. 2013). Kijjanapanich et al. (2013) found that the treated sand debris contained 0.3–0.7 g sulphate kg^{-1} sand, which is far below the Dutch government limit for the maximum amount of sulphate present in building sand and could thus be reused in construction activities.

Although sulphate was removed from the leachate, high calcium concentrations still remain in solution. High calcium concentrations may inhibit sulphate reduction (Kaksonen and Puhakka 2007). Calcium ions do not cause direct toxicity, but calcium carbonate precipitates can coat biomass, which hinders the substrate assimilation (Kaksonen and Puhakka 2007). Therefore, a calcium recovery step might be required in the process to prevent accumulation of calcium carbonate precipitates in the piping or the granular sludge, e.g. by chemical precipitation or microbial carbonate precipitation using ureolytic bacteria (Hammes et al. 2003; Whiffin et al. 2007; Al-Thawadi 2011; Al-Thawadi and Cord-Ruwisch 2012).

In the direct treatment concept, the solid waste is directly mixed with the electron donor in a column that functions both as leaching column and bioreactor (Hiligsmann et al. 1996; Kaufman et al. 1996; Kijjanapanich et al. 2014c) (Fig. 4.3b). The applicability of this direct approach depends on the gypsum content in the solid waste. The sulphide produced from this biological process can be recovered as elemental sulphur (S^0) (Dutta et al. 2008; Pikaar et al. 2011; Sahinkaya et al. 2011b) or sulphuric acid (Laursen and Karavanov 2006).

4.3.2 Sulphide Production Using Sulphate Reducing Bacteria

The carbon source and electron donor is the primary substrate required for sulphate reduction using sulphate reducing bacteria (Liamleam and Annachhatre 2007). Due to the low amounts of organic carbon in the sand debris leachate (Kijjanapanich et al. 2013), an external carbon source needs to be supplied to support sulphate reducing bacteria activity and growth. Organic waste can be an interesting option, because many companies have such waste streams. A disadvantage is, however, the possible need for a post-treatment step to remove the residual pollution or unwanted waste compounds from the organic waste itself (Kijjanapanich et al. 2013).

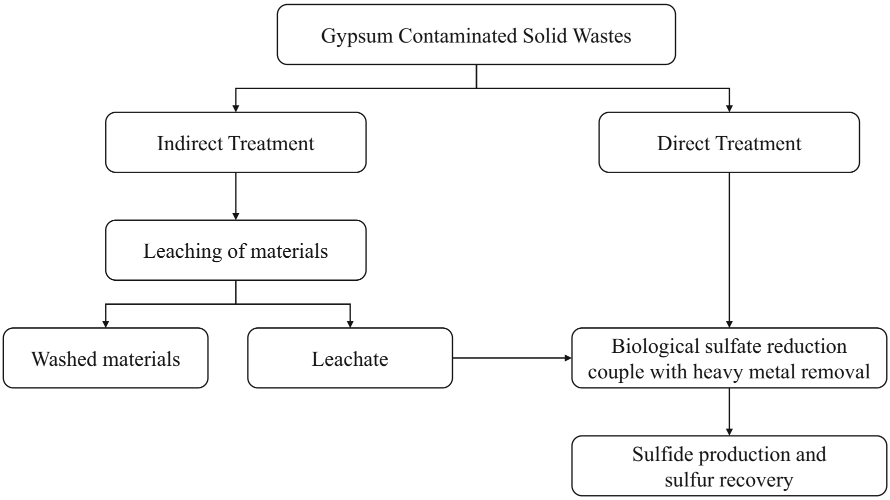

Fig. 4.2 Treatment concept for gypsum contaminated solid waste (Kijjanapanich et al. 2014c)

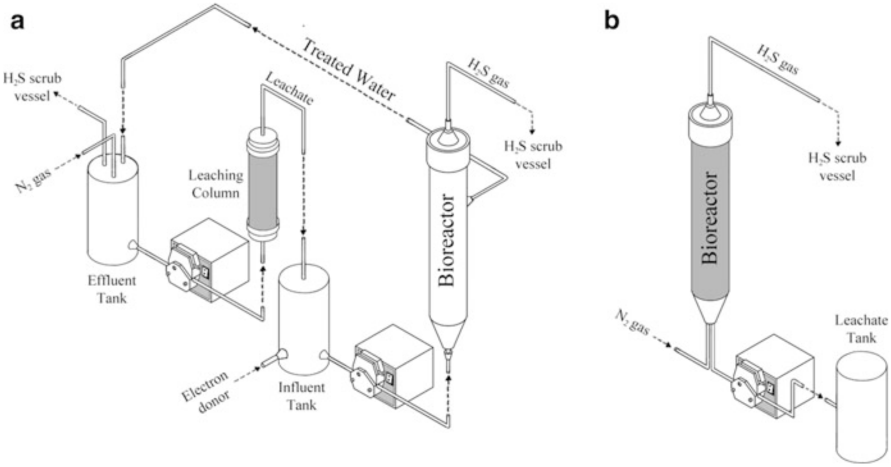

Fig. 4.3 Treatment for gypsum contaminated solid waste: (**a**) indirect treatment and (**b**) direct treatment. (■) indicates the location of the solid debris in the system

At the higher concentrations of solid wastes containing gypsum, sulphate reducing bacteria growth could be inhibited (Rzeczycka et al. 2004; Azabou et al. 2005), due to an accumulation of toxic levels of impurities, especially fluorine and heavy metals (Rzeczycka et al. 2004). Heavy metals, such as aluminium, arsenic, cadmium, chromium and copper, can inhibit the growth rate of sulphate reducing bacteria (Rzeczycka et al. 2004; Townsend et al. 2004; Azabou et al. 2005), depending on their speciation and concentration. Further studies are needed to reduce the toxicity of metals, radioactive and polycyclic aromatic hydrocarbons compounds present in these solid wastes to sulphate reducing bacteria.

In order to control the formation of desirable end products in sulphate reduction systems, process control which has been used for several biological production processes can be applied (Dunn et al. 2005; Villa-Gomez et al. 2014). With better process control, excess sulphide or dissolved organic carbon can be avoided (Cassidy et al. 2015), thus decreasing of the operational costs and eliminating the need for a post-treatment step.

4.3.3 Sulphide Removal from Sulphate Reducing Bioreactor Effluent

In the bioreactor treating solid waste containing gypsum, high sulphide concentrations can accumulate especially in full scale applications operated a high sulphate loading rate. The removal of sulphide from the system as well as the effluent of the biological sulphate reduction process is required, as sulphide can give an adverse effect to sulphate reducing bacteria in the system (Al-Zuhair et al. 2008) and cause several environmental impacts (Lens and Kuenen 2001; Vincke et al. 2001) or be re-oxidised to sulphate if directly discharged into the environment.

Metal sulphide precipitation (Eq. 4.5), particularly iron sulphide, is the common chemical process for sulphide removal (Firer et al. 2008; Nielsen et al. 2008; Zhang et al. 2009). Nowadays, biological sulphide oxidation using oxygen as electron acceptor and sulphide oxidising bacteria as a catalyst are used ubiquitous for the partial oxidation of H_2S to S^0 (Henshaw and Zhu 2001; Krishnakumar et al. 2005; González-Sánchez and Revah 2009; Sahinkaya et al. 2011b). However, this system requires energy for oxygen supply (van den Ende et al. 1996; Syed et al. 2006) and requires stringent process control (Syed et al. 2006). The pH in these biological systems is usually neutral or acidic (Gabriel and Deshusses 2003; Kraakman 2003). Moreover, the oversupply of oxygen yields a lower sulphate removal efficiency since most sulphide is converted to sulphate instead of elemental sulphur (Janssen et al. 1995).

In fact, either chemical or biological processes can be applied for sulphide oxidation to elemental sulphur (González-Sánchez and Revah 2007) and the reaction can occur either in acid or base conditions (Eqs. 4.6 and 4.7):

$$\text{Acid solution}: \quad H_2S_{(g)} \rightarrow S_{(s)} + 2H^+{}_{(aq)} + 2e^- \tag{4.6}$$

$$\text{Base solution}: \quad S^{2-}{}_{(aq)} \rightarrow S_{(s)} + 2e^- \tag{4.7}$$

Electrochemical treatment of sulphide rich wastewaters can be an appropriate way which offers several advantages, including good energetic efficiency, environmental compatibility, versatility, selectivity and cost effectiveness (Ángela et al. 2009; Dutta et al. 2009). Especially a spontaneous reaction or a galvanic cell, which not only removes sulphide, but also recovers sulphur as elemental sulphur and produces electricity is an attractive sulphide treatment option (Dutta et al. 2008; Kijjanapanich et al. 2015). A spontaneous electrochemical sulphide oxidation/ vanadium(V) reduction cell with graphite electrode system was reported for recovery of sulphide as elemental sulphur (Kijjanapanich et al. 2015).

4.4 Conclusions

Construction and demolition debris containing sulphate is an important source of pollution, which can create a lot of environmental problems, especially during disposal management at landfill sites. Although this debris can be reused as soil amendment or to make building materials, a concern has been raised by regulators regarding the chemical characteristics of the material and the potential risks to human health. Therefore, reduction of the sulphate and heavy metal content of debris before reuse is an option to overcome the above mentioned problems. Both chemical and biological processes can be used for sulphate and heavy metal removal. Biological sulphate removal using sulphate reducing bacteria coupled to metal precipitation can be applied for treatment of sulphate containing debris. The recovery of elemental sulphur, by either chemical or biological process, can also be achieved using this process. However, this debris has a low organic matter content, thus the addition of organic substrates as electron donor is necessary.

References

Al-Thawadi SM (2011) Ureolytic bacteria and calcium carbonate formation as a mechanism of strength enhancement of sand. J Adv Sci Eng Res 1(1):98–114

Al-Thawadi S, Cord-Ruwisch R (2012) Calcium carbonate crystals formation by ureolytic bacteria isolated from Australian soil and sludge. J Adv Sci Eng Res 2(1):12–26

Al-Zuhair S, El-Naas MH, Al-Hassani H (2008) Sulfate inhibition effect on sulfate reducing bacteria. J Biochem Technol 1(2):39–44

Ángela A, Ane U, Inmaculada O (2009) Contributions of electrochemical oxidation to waste-water treatment: fundamentals and review of applications. J Chem Technol Biotechnol 84 (12):1747–1755. doi:10.1002/jctb.2214

Annachhatre AP, Suktrakoolvait S (2001) Biological sulfate reduction using molasses as a carbon source. Water Environ Res 73(1):118–126. doi:10.2175/106143001X138778

Azabou S, Mechichi T, Sayadi S (2005) Sulfate reduction from phosphogypsum using a mixed culture of sulfate-reducing bacteria. Int Biodeterior Biodegrad 56(4):236–242. doi:10.1016/j.ibiod.2005.09.003

Azabou S, Mechichi T, Sayadi S (2007) Zinc precipitation by heavy-metal tolerant sulfate-reducing bacteria enriched on phosphogypsum as a sulfate source. Miner Eng 20:173–178. doi:10.1016/j.mineng.2006.08.008

Benatti CT, Tavares CRG, Lenzi E (2009) Sulfate removal from waste chemicals by precipitation. J Environ Manag 90(1):504–511. doi:10.1016/j.jenvman.2007.12.006

Benner SG, Blowes DW, Gould WD, Herbert RB, Ptacek CJ (1999) Geochemistry of a permeable reactive barrier for metals and acid mine drainage. Environ Sci Technol 33(16):2793–2799. doi:10.1021/es981040u

Bosman DJ, Clayton JA, Maree JP, Adlem CJL (1990) Removal of sulphate from mine water with barium sulphide. Mine Water Environ 9:149–163. doi:10.1007/BF02503689

California Contra Costa County (2013) Construction and demolition debris recovery program. http://www.cccounty.us/4746/CalGreen-Construction-Demolition-Debris-. Accessed Nov 2016

Cassidy J, Lubberding HJ, Esposito G, Keesman KJ, Lens PNL (2015) Automated biological sulphate reduction: a review on mathematical models, monitoring and bioprocess control. FEMS Microbiol Rev 39(6):823–853. doi:10.1093/femsre/fuv033

Castillo J, Pérez-López R, Sarmiento AM, Nieto JM (2012) Evaluation of organic substrates to enhance the sulfate-reducing activity in phosphogypsum. Sci Total Environ 439:106–113. doi:10.1016/j.scitotenv.2012.09.035

Costa MC, Martins M, Jesus C, Duarte JC (2007) Treatment of acid mine drainage by sulfate-reducing bacteria using low cost matrices. Water Air Soil Pollut 189(1–4):149–162. doi:10.1007/s11270-007-9563-1

Dar SA, Stams AJ, Kuenen JG, Muyzer G (2007) Co-existence of physiologically similar sulfate-reducing bacteria in a full-scale sulfidogenic bioreactor fed with a single organic electron donor. Appl Microbiol Biotechnol 75(6):1463–1472. doi:10.1007/s00253-007-0968-y

de Vries E (2006) Biological sulfate removal from construction and demolition debris sand. Wageningen University, Wageningen

Delaware Solid Waste Authority (2008) Construction and demolition (C&D) debris http://www.dswa.com/programs_construction.asp. Accessed Jan 2011

Dunn IJ, Heinzle E, Ingham J, Přenosil JE (2005) Biological reaction engineering. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Dutta PK, Rabaey K, Yuan Z, Keller J (2008) Spontaneous electrochemical removal of aqueous sulfide. Water Res 42:4965–4975. doi:10.1016/j.watres.2008.09.007

Dutta PK, Rozendal RA, Yuan Z, Korneel R, Keller J (2009) Electrochemical regeneration of sulfur loaded electrodes. Electrochem Commun 11:1437–1440. doi:10.1016/j.elecom.2009.05.024

Elliott P, Ragusa S, Catcheside D (1998) Growth of sulfate-reducing bacteria under acidic conditions in an upflow anaerobic bioreactor as a treatment system for acid mine drainage. Water Res 32(12):3724–3730. doi:10.1016/S0043-1354(98)00144-4

Firer D, Friedler E, Lahav O (2008) Control of sulfide in sewer system by dosage of iron salts: comparison between theoretical and experiment results, and practical. Sci Total Environ 392(1):145–156. doi:10.1016/j.scitotenv.2007.11.008

Gabriel D, Deshusses MA (2003) Performance of a full-scale biotrickling filter treating H_2S at a gas contact time of 1.6 to 2.2 s. Environ Prog 22(2):111–118. doi:10.1002/ep.670220213

Gibert O, de Pablo J, Cortina JL, Ayora C (2004) Chemical characterization of natural organic substrates for biological mitigation of acid mine drainage. Water Res 38:4186–4196. doi:10.1016/j.watres.2004.06.023

González-Sánchez A, Revah S (2007) The effect of chemical oxidation on the biological sulfide oxidation by an alkaliphilic sulfoxidizing bacterial consortium. Enzyme Microb Technol 40:292–298. doi:10.1016/j.enzmictec.2006.04.017

González-Sánchez A, Revah S (2009) Biological sulfide removal under alkaline and aerobic conditions in a packed recycling reactor. Water Sci Technol 59(7):1415–1421. doi:10.2166/wst.2009.121

Gypsum Association (1992a) Treatment and disposal of gypsum board waste: industry position paper. AWIC's Construction Dimensions, Construction Dimensions/February, AWIC, pp 5–6, 29–30

Gypsum Association (1992b) Treatment and disposal of gypsum board waste: technical paper part II. Construction Dimensions/March, AWIC, pp 58, 60–63

Hammes F, Seka A, de Knijf S, Verstraete W (2003) A novel approach to calcium removal from calcium-rich industrial wastewater. Water Res 37(3):699–704. doi:10.1016/S0043-1354(02)00308-1

Henshaw PF, Zhu W (2001) Biological conversion of hydrogen sulphide to elemental sulphur in a fixed-film continuous flow photo-reactor. Water Res 35(15):3605–3610. doi:10.1016/S0043-1354(01)00082-3

Hiligsmann S, Deswaef S, Taillieu X, Crine M, Milande N, Thonart P (1996) Production of sulfur from gypsum as an industrial by-product. Appl Biochem Biotechnol 57–58:959–969. doi:10.1007/BF02941776

Hlabela P, Maree J, Bruinsma D (2007) Barium carbonate process for sulphate and metal removal from mine water. Mine Water Environ 26:14–22. doi:10.1007/s10230-007-0145-7

Hulshoff Pol LW, Lens PNL, Stams AJM, Lettinga G (1998) Anaerobic treatment of sulphate-rich wastewaters. Biodegradation 9:213–224. doi:10.1023/A:1008307929134

Huttagosol P, Kijjamapanich V (2008) Active chemical treatment of water in the open pit of Ban Hong coal mine. In: The 2nd international workshop and conference on earth resources technology: stepping towards sustainable mining, Metallurigical and Petroleum Technology Development, Chulalongkorn University, Thailand, pp 83–88

Jang Y (2000) A study of construction and demolition waste leachate from laboratory landfill simulators. University of Florida, Gainesville

Jang YC, Townsend T (2001a) Sulfate leaching from recovered construction and demolition debris fines. Adv Environ Res 5:203–217. doi:10.1016/S1093-0191(00)00056-3

Jang YC, Townsend TG (2001b) Occurrence of organic pollutants in recovered soil fined from construction and demolition waste. Waste Manag 21:703–715. doi:10.1016/S0956-053X(01)00007-1

Janssen AJH, Sleyster R, van der Kaa C, Jochemsen A, Bontsema J, Lettinga G (1995) Biological sulphide oxidation in a fed-batch reactor. Biotechnol Bioeng 47(3):327–333. doi:10.1002/bit.260470307

Jong T, Parry DL (2003) Removal of sulfate and heavy metals by sulfate-reducing bacteria in short term bench scale upflow anaerobic packed bed reactor runs. Water Res 37:3379–3389. doi:10.1016/S0043-1354(03)00165-9

Kaksonen AH, Puhakka JA (2007) Sulfate reduction based bioprocesses for the treatment of acid mine drainage and the recovery of metals. Eng Life Sci 7(6):541–564. doi:10.1002/elsc.200720216

Kaufman EN, Little MH, Selvaraj PT (1996) Recycling of FGD gypsum to calcium carbonate and elemental sulfur using mixed sulfate-reducing bacteria with sewage digest as a carbon source. J Chem Technol Biotechnol 66:365–374. doi:10.1002/(SICI)1097-4660(199608)66:4<365::AID-JCTB520>3.0.CO;2-1

Kijjanapanich P, Pakdeerattanamint K, Lens PNL, Annachhatre AP (2012) Organic substrates as electron donors in permeable reactive barriers for removal of heavy metals from acid mine drainage. Environ Technol 33(23):2635–2644. doi:10.1080/09593330.2012.673013

Kijjanapanich P, Annachhatre AP, Esposito G, van Hullebusch ED, Lens PNL (2013) Biological sulfate removal from gypsum contaminated construction and demolition debris. J Environ Manag 131:82–91. doi:10.1016/j.jenvman.2013.09.025

Kijjanapanich P, Annachhatre AP, Esposito G, Lens PNL (2014a) Chemical sulphate removal for treatment of construction and demolition debris leachate. Environ Technol 35(16):1989–1996. doi:10.1080/09593330.2014.889219

Kijjanapanich P, Annachhatre AP, Esposito G, Lens PNL (2014b) Use of organic substrates as electron donors for biological sulfate reduction in gypsiferous mine soils from Nakhon Si Thammarat (Thailand). Chemosphere 101:1–7. doi:10.1016/j.chemosphere.2013.11.026

Kijjanapanich P, Annachhatre AP, Lens PNL (2014c) Biological sulfate reduction for treatment of gypsum contaminated soils, sediments and solid wastes. Crit Rev Environ Sci Technol 44:1037–1070. doi:10.1080/10643389.2012.743270

Kijjanapanich P, Do AT, Annachhatre AP, Esposito G, Yeh DH, Lens PNL (2014d) Biological sulfate removal from construction and demolition debris leachate: effect of bioreactor configuration. J Hazard Mater 269:38–44. doi:10.1016/j.jhazmat.2013.10.015

Kijjanapanich P, Kijjanapanich P, Annachhatre AP, Esposito G, Lens PNL (2015) Spontaneous electrochemical treatment for sulfur recovery by a sulfide oxidation/vanadium(V) reduction galvanic cell. J Environ Manag 149:263–270. doi:10.1016/j.jenvman.2014.10.024

Kraakman NJR (2003) Robustness of a full-scale biological system treating industrial CS_2 emissions. Environ Prog 22(2):79–85. doi:10.1002/ep.670220209

Krishnakumar B, Majumdar S, Manilal VB, Haridas A (2005) Treatment of sulphide containing wastewater with sulphur recovery in a novel reverse fluidzed loop reactor (RFLR). Water Res 39(4):639–647. doi:10.1016/j.watres.2004.11.015

Laursen JK, Karavanov AN (2006) Processes for sulfur recovery, regeneration of spent acid, and reduction of NO_x emissions. Chem Pet Eng 42(5–6):229–234. doi:10.1007/s10556-006-0084-3

Lee M, Kim J (2009) Membrane autopsy to investigate $CaCO_3$ scale formation in pilot-scale, submerged membrane bioreactor treating calcium-rich wastewater. J Chem Technol Biotechnol 84(9):1397–1404. doi:10.1002/jctb.2195

Lens PNL, Kuenen JG (2001) The biological sulfur cycle: novel opportunities for environmental biotechnology. Water Sci Technol 44(8):57–66

Lettinga G, van Velsen AFM, Hobma SW, de Zeeuw WJ, Klapwijk A (1980) Use of the upflow sludge blanket (USB) reactor concept for biological wastewater treatment, especially anaerobic treatment. Biotechnol Bioeng 22(4):699–734. doi:10.1002/bit.260220402

Liamleam W (2007) Zinc removal from industrial discharge using thermophilic biological sulfate reduction with molasses as electron donor. Asian Institute of Technology, Pathum Thani

Liamleam W, Annachhatre AP (2007) Electron donors for biological sulfate reduction. Biotechnol Adv 25(5):452–463. doi:10.1016/j.biotechadv.2007.05.002

Maree JP, Hlabela P, Nengovhela R, Geldenhuys AJ, Mbhele N, Nevhulaudzi T, Waamders FB (2004) Treatment of mine water for sulphate and metal removal using barium sulphide. Mine Water Environ 23:195–203. doi:10.1007/s10230-004-0062-y

Montero A, Tojo Y, Matsuto T, Yamada M, Asakura H, Ono Y (2010) Gypsum and organic matter distribution in a mixed construction and demolition waste sorting process and their possible removal from outputs. J Hazard Mater 175:747–753. doi:10.1016/j.jhazmat.2009.10.072

Morrison SJ, Spangler RR (1992) Extraction of uranium and molybdenum from aqueous solutions: a survey of industrial materials for use in chemical barriers for uranium mill tailings remediation. Environ Sci Technol 26(10):1922–1931. doi:10.1021/es00034a007

Morrison SJ, Spangler RR (1993) Chemical barriers for controlling groundwater contamination. Environ Prog 12:175–181. doi:10.1002/ep.670120305

Mulopo J, Ikhu-Omoregbe D (2012) Phosphogypsum conversion to calcium carbonate and utilization for remediation of acid mine drainage. J Chem Eng Process Technol 3(2). doi:10.4172/2157-7048.1000129

Nadagouda MN, Pressman J, White C, Speth TF, McCurry DL (2011) Novel thermally stable poly (vinyl chloride) composites for sulfate removal. J Hazard Mater 188:19–25. doi:10.1016/j.jhazmat.2011.01.005

Nevatalo LM, Makinen AE, Kaksonen AH, Puhakka JA (2010) Biological hydrogen sulfide production in an ethanol-lactate fed fluidized-bed bioreactor. Bioresour Technol 101:276–284. doi:10.1016/j.biortech.2009.07.042

Ngwenya EG, Walsh M, Metosh-Dickey CA, Portier RJ (2006) Remediation of acid mine drainage leachate by a physicochemical and biological treatment-train approach. Remediat J 16 (2):79–90. doi:10.1002/rem.20082

Nielsen AH, Hvitved-Jacobsen T, Vollertsen J (2008) Effects of pH and iron concentration on sulfide precipitation in wastewater collection systems. Water Environ Res 80(4):380–384

Ozacar M, Sengil IA, Turkmenler H (2008) Equilibrium and kinetic data, and adsorption mechanism for adsorption of lead onto valonia tannin resin. Chem Eng J 143:32–42. doi:10.1016/j.cej.2007.12.005

Pikaar I, Rozendal RA, Yuan Z, Keller J, Rabaey K (2011) Electrochemical sulfide removal from synthetic and real domestic wastewater at high current densities. Water Res 45:2281–2289. doi:10.1016/j.watres.2010.12.025

Plaza C, Xu Q, Townsend T, Bitton G, Booth M (2007) Evaluation of alternative landfill cover soils for attenuating hydrogen sulfide from construction and demolition (C&D) debris landfills. J Environ Manag 84:314–322. doi:10.1016/j.jenvman.2006.06.001

Rutherford PM, Dudas MJ, Arocena JM (1995) Radioactivity and elemental composition of phosphogypsum produced from three phosphate rock sources. Waste Manag Res 13:407–423. doi:10.1016/S0734-242X(05)80021-7

Rzeczycka M, Suszek A, Blaszczyk M (2004) Biotransformation of phosphogypsum by sulphate-reducing bacteria in media containing different zinc salts. Pol J Environ Stud 13(2):209–217

Sahinkaya E, Gunes FM, Ucar D, Kaksonen AH (2011a) Sulfidogenic fluidized bed treatment of real acid mine drainage water. Bioresour Technol 102:683–689. doi:10.1016/j.biortech.2010.08.042

Sahinkaya E, Hasar H, Kaksonen AH, Rittmamm BE (2011b) Performance of a sulfide-oxidizing, sulfur-producing membrane biofilm reactor treating sulfide-containing bioreactor effluent. Environ Sci Technol 45(9):4080–4087. doi:10.1021/es200140c

Shaw WA (2008) Benefits of evaporation FGD purge water. US. EPA. https://www3.epa.gov/region1/npdes/merrimackstation/pdfs/ar/AR-149.pdf. Accessed in Nov 2016

Silva AJ, Varesche MB, Foresti E, Zaiat M (2002) Sulphate removal from industrial wastewater using a packed-bed anaerobic reactor. Process Biochem 37:927–935. doi:10.1016/S0032-9592(01)00297-7

Singh M, Garg M (2000) Making of anhydrite cement from waste gypsum. Cem Concr Res 30 (4):571–577. doi:10.1016/S0008-8846(00)00209-X

Syed M, Soreanu G, Falletta P, Beland M (2006) Removal of hydrogen sulfide from gas streams using biological processes-a review. Can Biosyst Eng 48:2.1–2.14

Taher MA (2007) Influence of thermally treated phosphogypsum on the properties of Portland slag cement. Resour Conserv Recycl 52(1):28–38. doi:10.1016/j.resconrec.2007.01.008

Tayibi H, Choura M, Lopez FA, Alguacil FJ, Lopez-Delgado A (2009) Environmental impact and management of phosphogypsum. J Environ Manag 90:2377–2386. doi:10.1016/j.jenvman.2009.03.007

Townsend T, Tolaymat T, Leo K, Jambeck J (2004) Heavy metals in recovered fines from construction and demolition debris recycling facilities in Florida. Sci Total Environ 332:1–11. doi:10.1016/j.scitotenv.2004.03.011

Turley W (1998) What's happening in gypsum recycling. C&D Debris Recycl 5(1):8–12

U.S.EPA (1998) Characterization of building-related construction and demolition debris in the United States. EPA 530-R-98-010, Washington, DC

U.S.EPA (2000) Wastewater technology fact sheet chemical precipitation. U.S.EPA , Washington, DC

U.S.EPA (2003) Estimating 2003 building-related construction and demolition materials amounts. U.S.EPA , Washington, DC

U.S.EPA (2008) Agricultural uses for flue gas desulfulfurization (FGD) gypsum. U.S.EPA, Washington, DC

Vallero MVG, Lettinga G, Lens PNL (2005) High rate sulfate reduction in a submerged anaerobic membrane bioreactor (SAMBaR) at high salinity. J Membr Sci 253(1–2):217–232. doi:10.1016/j.memsci.2004.12.032

van den Ende FP, Laverman AM, van Gemergen H (1996) Coexistence of aerobic chemotrophic and anaerobic phototrophic sulfur bacteria under oxygen limitation. FEMS Microbiol Ecol 19 (3):141–151. doi:10.1016/0168-6496(95)00082-8

Veeken AHM, Rulkens WH (2003) Innovative developments in the selective removal and reuse of heavy metals from wastewaters. Water Sci Technol 47:9–16

Villa-Gomez D, Ababneh H, Papirio S, Rousseau DPL, Lens PNL (2011) Effect of sulfide concentration on the location of the metal precipitates in inversed fluidized bed reactors. J Hazard Mater 192:200–207. doi:10.1016/j.jhazmat.2011.05.002

Villa-Gomez DK, Cassidy J, Keesman KJ, Sampaio R, Lens PNL (2014) Sulfide response analysis for sulfide control using a pS electrode in sulfate reducing bioreactors. Water Res 50:48–58. doi:10.1016/j.watres.2013.10.006

Vincke E, Boon N, Verstraete W (2001) Analysis of the microbial communities on corroded concrete sewer pipes – a case study. Appl Microbiol Biotechnol 57:776–785. doi:10.1007/s002530100826

Waybrant KR, Blowes DW, Ptacek CJ (1998) Selection of reactive mixtures for use in permeable reactive walls for treatment of mine drainage. Environ Sci Technol 32(13):1972–1979. doi:10.1021/es9703335

Whang JS, Young D, Pressman M (1982) Soluble-sulfide precipitation for heavy metals removal from wastewaters. Environ Prog 1:110–113. doi:10.1002/ep.670010212

Whiffin VS, van Paassen LA, Harkes MP (2007) Microbial carbonate precipitation as a soil improvement technique. Geomicrobiol J 24:417–423. doi:10.1080/01490450701436505

Wolicka D, Borkowski A (2009) Phosphogypsum biotransformation in cultures of sulphate reducing bacteria in whey. Int Biodeterior Biodegrad 63:322–327. doi:10.1016/j.ibiod.2008.09.011

Wolicka D, Kowalski W (2006) Biotransformation of phosphogypsum in petroleum-refining wastewaters. Pol J Environ Stud 15(2):355–360

Zhang L, Keller J, Yuan Z (2009) Inhibition of sulfate-reducing and methanogenic activites of anaerobic sewer biofilms by ferric iron dosing. Water Res 43(17):4123–4132. doi:10.1016/j.watres.2009.06.013

Zhao Y, Chen C, Han Y (2010) Study on treating desulfurization gypsum by sulfate-reducing bacteria. J Environ Technol Eng 3(1):5–10

Chapter 5
Lead and Zinc Metallurgical Slags Mineralogy and Weathering

Nang-Htay Yin, Piet N.L. Lens, Yann Sivry, and Eric D. van Hullebusch

Abstract Base-metal smelters typically produce a large quantity of waste rocks, tailings and slags that are usually stored on site. In the early 1980s, metallurgical slags were considered chemically inert because metals are usually embedded in glass and silicate phases. Recently, several studies showed that metals leaching from slag dumps can lead to severe contamination of soils and water bodies. Predicting their environmental impact requires an understanding of the minerals at microscopic scales as well as the mineral-water interactions, i.e. the chemical and biological weathering techniques applied, the associated weathering rates and mechanisms.

Both lead and zinc slags are chemically and mineralogically diverse, depending on the smelting history (i.e. the mother ores), the smelting technologies and the flux minerals. The Pb and Zn concentration in slags indicates the recovery efficiency of the smelting technologies, the presence of S indicates if the mother ores are rich in either sulphides or carbonates, and the proportion of Ca, Fe and Si reflects the type of flux minerals added to decrease the viscosity of the melt. Similarly, the presence of the pyroxene group indicates a relatively slow cooling regime whereas the presence of amorphous glass indicates the rapid cooling of the slags. The presence of Fe oxides such as goethite or hematite on the top layer of the slags indicates the slag dump being weathered for some time.

N.-H. Yin
Université Paris-Est, Laboratoire Géomatériaux et Environnement (EA 4508), UPEM, 77454 Marne-la-Vallée, cedex 2, France

P.N.L. Lens
UNESCO-IHE Institute for Water Education, Delft, The Netherlands

Department of Chemistry and Bioengineering, Tampere University of Technology, PO Box 10541, Tampere, Finland

Y. Sivry
Institut de Physique du Globe de Paris, Sorbonne Paris Cité, Univ. Paris Diderot, UMR 7154, CNRS, F-75005 Paris, France

E.D. van Hullebusch (✉)
Université Paris-Est, Laboratoire Géomatériaux et Environnement (LGE), EA 4508, UPEM, 77454 Marne-la-Vallée, France

UNESCO-IHE Institute for Water Education, Delft, The Netherlands
e-mail: Eric.vanHullebusch@univ-paris-est.fr

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Chemical alteration studies of slags focus on different experimental conditions such as the contact time, type of leachant, agitation rate, pH, liquid to solid (L/S) ratios, and particle size of the sample. The chemical protocol tests are batch tests, quick and simple to carry out with reproducible results, and they can give an idea of the leaching behaviour of metals under different leaching scenarios such as landfill, acid rain or soil dumping. On the other hand, there are only a few studies for biological alteration of slags in spite of the fact that the presence of microbial activity increases the dissolution rate of slags. Therefore, combining and enhancing the performance of both chemical and biological leaching reveals the great potential of metal mining and recovery of base metals from Pb and Zn metallurgical slags.

Keywords Metallurgical slags • Alteration • Weathering • Heavy metals mobilisation • Leaching • Secondary precipitates formation

Contents

Abbreviations

ANC	Acid neutralising capacity
Ano	Anorthite
$CaCO_3$	Calcium carbonate
Clif	Clinoferrosilite
CliPy	Clinopyroxene
Cu-Zn slags	Slags from a mixture of zinc and copper smelter
EINECS	European Inventory of Existing Commercial Substances
EN 12457-2	Euronorm leaching test
EPS	Extracellular polymeric substances

Fr	Franklinite
Gah	Gahnite
Gl	Glass
Gn	Galena
Ha	Hardystonite
He	Hedenbergite
Hya	Hyalophane
Kfel	K-feldspar
Kir	Kirschsteinite
La	Labradorite
LBF	Lead slags from lead blast furnace
Leu	Leucite
Me	Melilite
Mg	Magnetite
MgCr	Magnesiochromite
Mul	Mullite
NEN 7341 test	Diffusion-leaching test developed by the Netherlands
Ol	Olivine
Pb slags	Slags from lead smelter
Pb-Cu slags	Slags from a mixture of lead and copper smelter
PbS	Lead sulfide
Pb-Si	Lead silicate
Pl	Plagioclase
Po	Pyrrhotite
Py	Pyroxene
S	Sulphur
SI	Saturation index
Spl	Spinel
SPLP	Synthetic precipitation leach procedure
SWEP	Special waste extraction procedure
TCLP	Standard toxicity characterisation leaching procedure
USEPA	United States Environmental Protection Agency
Wil	Willemite
Wo	Wollastonite
Zn slags	Slags from zinc smelter
Znc	Zincite
ZnCr	Zincochromite
ZnS	Zinc sulfide

5.1 Metallurgical Slags

Metallurgical slags are predominantly vitreous by-products derived from the smelting of metallic ores and usually consist of metal silicates and oxides, and in some cases also sulphides and native metals (Hudson-Edwards et al. 2011). Slags are the wastes whose grade is too low for further treatment and which are of too low economic value in spite of being generated in great amounts by the mining industry. They are either dumped in the vicinity of the mining site and accumulated for long periods of time or reused as fill, ballast, abrasive and aggregate in concrete and cement production, and in road construction (Ettler and Johan 2003; Lottermoser 2002; Potysz et al. 2015). Ferrous slags from iron and steel industries are reused in construction (Saikia et al. 2012), whereas reuse of non-ferrous slags from lead, zinc, copper, nickel, and chromium industries is limited till now (Barna et al. 2004).

Slags derived from the processing and smelting of lead (Pb) and zinc (Zn) are defined as 'hazardous waste' by the European Waste Catalogue (Commission Decision 94/3/EC), but also as a 'commercial substance' by the European Inventory of Existing Commercial Substances (EINECS) adopted by Council Regulation no. 793/93 (Ettler et al. 2001, 2003). Many studies have already shown that Pb and Zn smelting activities are large contributors of anthropogenic Pb and Zn pollution in many environmental compartments: atmospheric heavy metal emissions and deposition (Van Alphen 1999), surface and ground water (Parsons et al. 2001), kitchen garden soil (Douay et al. 2008), woody habitat soil (Douay et al. 2009), agricultural topsoil (Pelfrene et al. 2011), river bank soil (Sivry et al. 2010), river and stream sediment (Audry et al. 2004; Vdovic et al. 2006; Yang et al. 2010) and seepage at slag dumps (Navarro et al. 2008) with a high potential of groundwater contamination, and evidence of high bio-accessibility of lead (Pb) and zinc (Zn) in the human body (Bosso and Enzweiler 2008; Ettler et al. 2012).

5.2 Composition of Slags

5.2.1 Chemical Composition

Slags are very heterogeneous materials where the chemical composition can be related to the smelting history, the constituents of the mother ores, the flux minerals (limestone, iron stone, ferrous silicate, silica) and fuels (coke, coal, firewood, charcoal) used (Lottermoser 2002). The chemical composition of lead and zinc slags from different countries is given in Table 5.1, whereas those generated during different time periods is given in Table 5.2.

Both Pb and Zn slags are chemically diverse materials where the lesser or higher concentration of Pb and Zn in the slags indicates the efficiencies of the smelting and processing technologies used in that particular country (Table 5.1). The enrichment of Ca, Fe and Si reflects the type of flux minerals added during smelting in order to lower the melting temperature as well as to modify the chemical properties, particularly to decrease the viscosity of the slags (Lottermoser 2002). In addition, the presence of Sulphur (S) in the slag indicates that the primary ores can be rich in sulphides rather than carbonates and oxides. The metals in slag melts can also be associated with the silicate phases, metallic droplets, and the leftover S in the form of sulphides (PbS, ZnS).

Table 5.1 Major and minor chemical composition of Pb-Zn slags from different countries

Unit (% wt)	Pb slags				Zn slags			
Origin of slags	France	Brazil	Czech Republic	Belgium	France	USA	Poland	UK
References	A, B, C	D	E	F	A, C	G	H	I
SiO_2	23.17–26.59	21.39	34.92	25.7	21.9–25.82	32.1–57.1	12.43–41.27	11.3–19.83
CaO	20.00–22.47	23.11	20.5	18.9	18.10–18.77	1.55–15.3	4.97–23.53	3.3–15.66
FeO and Fe_2O_3	31.01–33.7	28.1	24.98	34	30.89–33.7	7.3–21.7	9.86–29.68	30.66–52.9
Al_2O_3	1.89–2.48	3.56	5.07	5.4	9.89–10.4	12.7–21.9	3.38–20.69	5.5–8.25
MgO	2.61–2.8	5.44	2.36	1.4	1.78–1.84	0.61–1.28	3.6–10.68	–
MnO	0.80–0.81	1.44	2.28	0.66	1.02–1.06	0.04–0.35	0.34–1.21	–
Na_2O	0.58–0.64	0.27	0.23	0.87	0.55–0.58	0.9–3.93	0–0.27	–
K_2O	0.27–0.38	0.26	0.97	0.31	0.68–0.7	1.23–3.91	0.18–0.95	–
TiO_2	0.19–0.2	0.25	0.59	–	0.48–0.49	0.64–1.14	0.13–0.89	–
P_2O_5	0.22–0.29	–	0.34	–	0.5–0.56	0.1–0.46	0.09–0.35	–
Zn	8.06–11.2	7.61	36300[a]	4.02	6.54–7.51	11.4–8960[a]	0.3–38.0	5.57–11.43
Pb	3.38–3.55	3.77	11223[a]	2.29	0.69–1.56	1.9–711[a]	0.15–6.20	0.57–6.87
S	0.19–0.7	0.37	1.11	–	1.05–1.58	0.08–2.68	0.41–2.23	1.77–4.11
Unit	**ppm**	**mg/kg**	**mg/kg**	**mg/kg**	**ppm**	**mg/kg**	–	–
Ag	12.1–13	–	–	–	44–45	1.0–10	–	–
As	717–780	541	264	4200	930–1210	1.0–32	–	–
Ba	5919–6500	169	1106	–	2410–2440	215–1170	–	–
Cr	908–965	71	36.8	1001	1460–1510	71–103	–	–
Ni	71–83	82.2	20.4	416	198–267	24.3–107	–	–
Mo	266–280	28.4	–	279	81–83	2.4–37.3	–	–
Cd	3.2–4	–	9.22	5.81	<0.5	0.8–48.1	–	–
Cu	1150–1250	538	969	–	2600–2900	16–6360	–	–

A: Deneele (2002), *B*: Seignez et al. (2007), *C*: Barna et al. (2004), *D*: de Andrade Lima and Bernardez (2011), *E*: Ettler et al. (2004), *F*: Saikia et al. (2008 and 2012), *G*: Piatak and Seal (2010), *H*: Puziewicz et al. (2007), *I*: Morrison et al. (2003)

[a] Zn and Pb in ppm unit. Note that ppm refers to water weight whereas mg/kg refers to solid weight

Table 5.2 Major chemical composition of historical smelting slags and slags from secondary processes

	Historical smelting slags				Slags from processing car batteries	
Unit (% wt)	3–4th century (France)	1901–1943 (Australia)	Sixteenth century (Sweden)	Middle ages (Czech republic)	Old tech	Modern tech
References	A	B	A	C	C	C
SiO_2	56.83	34.8	61.28	39.19	29.32	30.06
CaO	15.69	15.53	24.06	3.23	19.79	21.8
FeO and Fe_2O_3	11.97	32.88	1.46	23.41	32.25	28.62
Al_2O_3	7.17	5.41	3.42	4.46	5.46	11.52
MgO	2.71	0.91	5.72	3.46	2.31	2.88
MnO	1.89	0.39	3.27	3.92	1.31	0.88
Na_2O	0.06	0.26	0.33	0.21	0.82	0.32
K_2O	3.34	0.6	0.51	1.42	0.21	0.11
TiO_2	0.43	–	0.02	0.41	0.3	0.48
P_2O_5	0.25	0.27	0	0.61	0.23	0.3
Zn	–	23643[a]	–	5.41	2.17	0.21
Pb	–	7605[a]	–	11.81	2.51	0.68
S	–	1.15	–	1.19	0.94	0.36

A: Mahé-Le Carlier et al. (2000), *B*: Lottermoser (2002), *C*: Ettler et al. (2000)
[a] Zn and Pb in ppm unit

The heterogeneous Pb and Zn slags can be further compared to historical slags and car battery processing slags (Table 5.2). Historical slags are most likely subjected to weathering over time, thereby studying of these slags in comparison to Pb/Zn slags as well as modern slags can give a very useful insight into the behavior of metal release over time. Historical slags originating from France and Sweden, generated around the 3–4th and sixteenth century respectively, show the highest content of Si and Ca, with relative deficiency in Fe content and the absence of Pb and Zn (Table 5.2). Slags produced during the Middle Ages in the Czech Republic are deficient in Ca compared to other slags, as $CaCO_3$ additives were introduced only later. On the other hand, the slags from secondary car batteries processing units and those from Australia, generated in the early twentieth century, or modern slags have a similar chemical composition of Si, Ca, and Fe, with relatively little amounts of Pb and Zn present. Thus, all historical slags produced before the nineteenth century have a similar chemical composition regardless of their native countries. The same goes for modern slags generated after the nineteenth century regardless of their native countries, as well as primary or secondary production sources.

5.2.2 Mineral Phases

Slags may possess many previously unknown mineral phases and their mineral species status cannot be identified because they are formed in a geologically modified environment under anthropogenic influences (Nickel 1995). As a result of quenching, slags can be mineralogically diverse, enriched in glass and crystalline phases. During smelting, both Pb and Zn ores are mixed with flux minerals and fuels on the charge floor inside the blast furnace. Oxygen is constantly provided by a blast of compressed air and the temperature inside the furnace reaches over 1500 °C. A lighter silicate melt accumulates over the liquid metal melt present at the bottom of the furnace. The above silicate melt is then drained off and cooled down under a massive shower of cold water.

As given in Table 5.3, Pb slags originating from France are mainly composed of non-silicate minerals such as the spinel group (magnesiochromite, franklinite, wüstite and magnetite) and other oxides (mixture of Zn and Fe oxides) as they contain only one silicate mineral, the melilite. In contrast, slags from Brazil and the Czech Republic show the presence of more silicate minerals: the olivine (fayalite and kirschsteinite), pyroxene (hedenbergite) and melilite (unidentified phase and willemite) group. Non-silicates have not been observed in the slags from the Czech Republic but these contain only substantial amounts of relict ores (galena, sphalerite, würzite and pyrrhotite).

As given in Table 5.4, Zn slags generated from France include only one silicate mineral (hardystonite), non-silicates group of spinel (wüstite), other oxides (mixture of Fe, Zn and Al), and traces of relict ores (wurzite and sphalerite). More diversity of silicates and oxides has been observed in slags from the USA and Poland. Slags from the USA contain the olivine (fayalite and olivine), pyroxene (clinoferrosilite and hedenbergite), feldspars (K-feldspar, hyalophane and labradorite), melilite (hardystonite) and alumino silicate (willemite, mullite, quartz and sillimanite) groups. Those from Poland contain olivine (kirschsteinite and olivine), pyroxene (wollastonite), feldspars (K-feldspar, hyalophane and leucite), melilite (melilite) and alumino silicate (willemite) groups.

5.2.3 Petrography

They are lustrous darker grey to brown in colour. The crystalline particles are 100 to 1000 μm in size across the slags (Puziewicz et al. 2007). The formation of mineral phases bears a direct relationship with the bulk composition of the melt and with the cooling regime, which controls the crystallization sequence in the slag. Slags can be classified into several assemblages based on their chemical and mineralogical composition.

Table 5.3 Primary mineral phases usually encountered in Pb slags described in the literature

			Origin		
Minerals	Primary phases	Composition	France	Brazil	Czech Republic
Silicate	Olivine group	Fayalite ($Fe^{2+}_2SiO_4$)			*
		Kirschsteinite ($CaFe^{2+}SiO_4$)		*	*
		Olivine [$(Ca,Fe)_2SiO_4$]		*	
		Willemite (Zn_2SiO_4)	*	*	
	Pyroxene group	Hedenbergite ($CaFe^{3+}Si_2O_6$)			*
	Melilite group	Ca_2 $(Fe,Mg,Zn,Al)(Al,Si)_2O_7$		*	*
Non-silicate	Spinel group	Spinel ($MgAl_2O_4$)		*	
		Magnesiochromite ($MgCr_2O_4$),	*		
		Franklinite [$(Zn,Mn^{2+},Fe^{2+})(Fe^{3+},Mn^{3+})_2O_4$]	*	*	
		Magnetite ($Fe^{3+}_2Fe^{2+}O_4$)	*		
	Other oxides	Zn substituted Wüstite ($Fe_{(0.85-x)}Zn_xO$)	*		
		Wüstite (FeO)	*	*	
		Iron(II) Chromate ($FeCrO_4$)	*		
		Magnetite (Fe_3O_4)	*		
		Zincite (ZnO)		*	
	Pure metals	Lead (Pb)	*	*	*
	Sulphides group	Galena (PbS)			*
		Wurzite (ZnS)			*
		Sphalerite (ZnS)			*
		Pyrrhotite ($Fe_{(1-x)}S$)			*
References			A	B	C

A: Seignez et al. (2007 and 2008), Deneele (2002), *B*: de Andrade Lima and Bernardez (2011), *C*: Ettler and Johan (2003), Ettler et al. (2001)

* occurence of the mentioned mineral

Assemblage I: Dark gray slag located outer cast of slag pile containing spinel, olivine, clinopyroxene and glass,

Assemblage II: Dark gray slag located central of slag pile containing spinel, melilite, olivine and glass,

Assemblage III: Red slag located on top of slag pile containing feldspar, quartz, mullite, glass, spinel, and secondary goethite, hematite and gypsum,

Assemblage IV: Green slag composed mainly of willemite, hardystonite, gahnite and zincite.

The assemblage I is from the outer cast of slag dumped where the presence of the pyroxene group indicates the relatively slow cooling regime. Assemblage II is located in the central part of the slag dump where the absence of pyroxene indicates

Table 5.4 Primary mineral phases usually encountered in Zn slags described in the literature

			Origin		
Minerals	Primary phases	Composition	France	USA	Poland
Silicate	Olivine group	Fayalite ($Fe^{2+}{}_2SiO_4$)		*	
		Kirschsteinite ($CaFe^{2+}SiO_4$)			*
		Olivine [$(Ca,Fe)_2SiO_4$]		*	*
		Willemite (Zn_2SiO_4)		*	*
	Pyroxene group	Wollastonite ($Ca_2Si_2O_6$)			*
		Clinoferrosilite ($Fe_2Si_2O_6$)		*	
		Hedenbergite ($CaFe^{3+}Si_2O_6$)		*	
	Feldspars	K-feldspar ($KAlSi_3O_8$)		*	*
		Hyalophane $(K,Ba)[Al(Si,Al)Si_2O_8]$		*	*
		Anorthite ($CaAl_2Si_2O_8$)		*	
		Labradorite $(Ca,Na)[Al(Al,Si)Si_2O_8]$		*	
		Leucite ($KAlSi_2O_6$)			*
	Melilite group	Hardystonite ($CaZnSi_2O_7$)	*	*	
	Alumino silicates	Mullite ($Al_6Si_2O_{13}$)		*	
		Sillimanite (Al_2SiO_5)		*	
Non-silicate	Spinel group	Spinel ($MgAl_2O_4$)		*	*
		Wüstite (FeO)	*		
	Other oxides	Zincite (ZnO)		*	*
		Quartz or Tridymite (SiO_2)		*	
		Magnetite (Fe_2O_3)		*	
		Goethite [$FeO(OH)$]		*	
	Pure metals	Fe, Ni, Pb	*	*	*
	Sulphides group	Würtzite (ZnS)	*	*	
		Sphalerite (ZnS)	*	*	
		Pyrrhotite ($Fe_{(1-x)}S$)			*
References			A	B	C

A: Deneele (2002), *B*: Piatak and Seal (2010), *C*: Puziewicz et al. (2007)
* occurence of the mentioned mineral

the rapid cooling (quenching effect) of the slag (Ettler et al. 2001). Being on the top of the slag pile, assemblage III is in constant exposure to water and the atmosphere, leading to the formation of secondary Fe oxides such as goethite, hematite and gypsum. A very different mineralogy of slag can be expected in the case of assemblage IV, which is enriched in Zn bearing phases such as willemite, hardystonite, gahnite and zincite (Piatak and Seal 2010).

Among all these assemblages, Zn and Pb are redistributed among several crystalline phases (silicates, oxides, sulfide or metallic phases) and residual glass. Zn, being dissolved in the silicate melt, is partially incorporated into the structures of oxides (spinels), silicates (clinopyroxene, melilite or olivine), sulphides

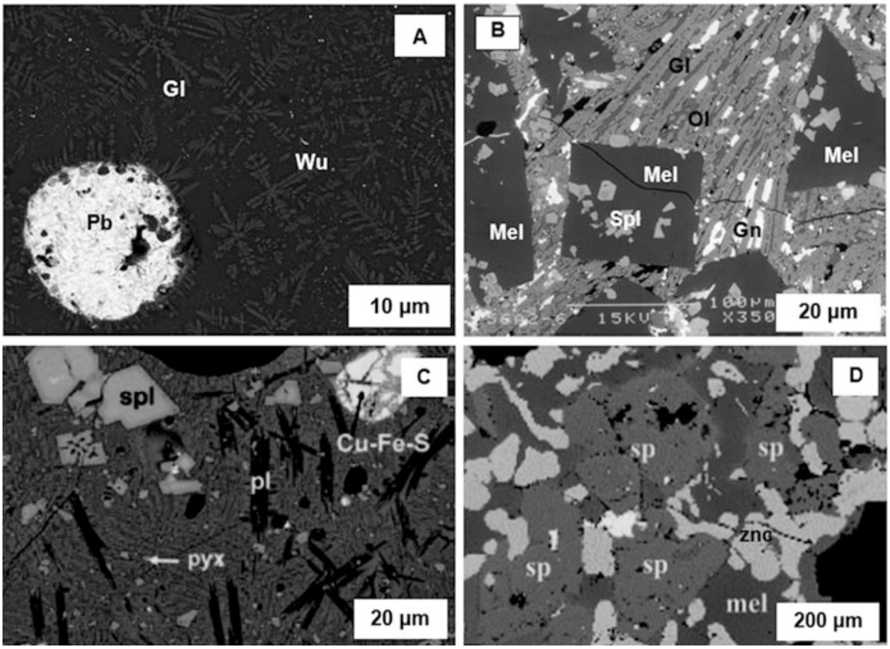

Fig. 5.1 Back-scattered electron images of Pb slags from France and the Czech Republic (**a** and **b**) and Zn slags from United States and Poland (**c** and **d**). (**a**): wustite (Wu), and metallic lead (Pb) embedded into the glass matrix (Gl) (van Hullebusch et al., unpublished picture). (**b**): prismatic crystals of melilite (Mel) including spinels (Spl), accompanied by long needles of olivine (Ol) and galena inclusions (Gn) inside glass (Gl) (Ettler et al. 2001). (**c**): skeletal plagioclase (Pl), spinels (Spl), Cu–Fe-sulfide blebs (Cu-Fe-S) with pyrrhotite (Po) in cracks, and dendritic pyroxene (Pyx) in matrix (Piatak and Seal 2010). (**d**): spinel (Spl), anhedral melilite (Mel) and zincite (Znc) embedded in matrix glass (Puziewicz et al. 2007)

(sphalerite or würtzite) and glass (Fig. 5.1). In contrast, Pb behaves as an incompatible element and is concentrated in residual glass and in Pb-rich sulfide or metallic inclusions trapped in the glass (Ettler et al. 2000, 2001).

5.2.4 Phase Composition

The olivine group is the most abundant crystalline phase found in slags which crystallised either early or as the last silicate filling spaces between the earlier-crystallised silicates (Ettler et al. 2001). It is present in different shapes such as a herring-bone pattern, in a thin-narrow-long strip laths pattern of several hundred of micrometers in length or very fine dendrites from several micrometers to tens of micrometers in size (Fig. 5.1). Olivine-group minerals are major Zn concentrators

Table 5.5 Microprobe studies of each mineral phase present in Pb slags

Minerals (% wt)	Glass	Silicates			Oxides		
	Gl	Ol	CliPy	Me	MgCr	Fr	Mg
SiO_2	26.4	29.66–32.89	39.87–43.34	38.62–39.98	0.28	0.10	0.05
TiO_2	0.2	0.00–0.06	0.25–1.03	0.00–0.06	0.61	0.09	0.34
Al_2O_3	2.5	0.01–0.74	4.73–11.2	3.48–5.09	15.83	0.62	7.60
Cr_2O_3	0.0	0.01–0.03	0.00	0.00–0.04	44.56	1.66	13.59
FeO	26.5	27.67–55.57	18.91–26.14	7.51–9.00	5.55	7.69	17.29
Fe_2O_3	–	–	–	–	8.95	67.62	45.45
CaO	22.9	2.77–27.48	20.59–22.62	34.11–37.28	0.57	0.68	0.13
MgO	1.9	0.85–5.33	0.19–2.41	1.82–4.45	12.46	4.83	1.99
MnO	0.8	2.13–5.91	0.62–1.8	0.04–1.06	0.79	0.91	0.74
ZnO	11.2	1.98–6.28	1.23–3.12	4.11–10.51	9.90	15.79	12.72
PbO	4.3	0.02–0.18	0.08–0.20	0.02–0.35	–	–	–
Na_2O	0.9	0.08–0.27	0.03–0.28	0.32–2.36	–	–	–
K_2O	0.4	0.03–0.14	0.01–0.26	0.08–0.69	–	–	–
References	A and C	B	B	B	C	C	C

Me Melilite, *Ol* Olivine, *Gl* Glass, *CliPy* Clinopyroxene, *Fr* Franklinite, *MgCr*Magnesiochromite, *Mg* Magnetite

A: Seignez et al. (2007), *B*: Ettler et al. (2001), *C*: Deneele (2002)

where the amount of Zn can be 1.98–6.28% in weight for Pb slags (Table 5.5) and 1.29% in weight for Zn slags (Table 5.6).

The clinopyroxene group is a QUAD pyroxene, i.e. a solid solution of $Mg_2[Si_2O_6]$ – $Fe_2[Si_2O_6]$ – $CaMg[Si_2O_6]$ – $CaFe[Si_2O_6]$ (Puziewicz et al. 2007). It can be found in both Pb and Zn slags, where the amount of Zn can vary from 0.1 to 4.8% in weight (Tables 5.5 and 5.6).

Feldspars are found only in Zn slags, indicating a high alkali content which originates from the limestone present in the primary ores. Primary crystallisation in the slag melt led to the formation of skeletal feldspars with spinifex texture (Piatak and Seal 2010). Silica was removed from the melt during the formation, leading to the absence of residual glass.

The melilite group is found abundantly in the Zn and Pb slags, either as irregular prisms with a star shape, as dendrites or as phenocrysts from 10–100 of micrometers in size. They are members of the åkermanite ($Ca_2Mg[Si_2O_7]$), the gehlenite ($Ca_2Al_2[SiO_7]$) solid solution series and their ferrous/ferric analogues (Puziewicz et al. 2007). They are main concentrators of Zn and Pb where hardystonite and willemite are major minerals found in both Pb and Zn slags (Tables 5.5, 5.6 and 5.7).

The spinel group is the first mineral phase formed in high-temperature silicate melts, where silicates nucleating simultaneously with the oxides usually enclose small crystals of spinel (Ettler et al. 2001). They can be found either in trace, abundant amount or generally as cubic or octahedral crystals several micrometers

Table 5.6 Microprobe studies of each mineral phase present in Zn slags

		Silicates									
	Glass	Olivine group		Pyroxene group			Feldspars				
Minerals (%wt)	Gl	Kir	Ol	Py and wo	He	Clif	Leu	K-fel	Hya	Ano	La
SiO_2	25.7	34.81	30.96–37.1	30.25	41.13	40.79	50.81	64.99	59.46	44.01	53.78
TiO_2	0.6	0.00	0.02–0.08	0.30	3.24	2	0.04	–	0.12	0.25	0.06
Al_2O_3	10.0	0.00	0–0.04	4.99	10.97	9.11	25.56	18.8	21.42	35.12	29.07
FeO and Fe_2O_3	25.0	23.01	25.8–64.46	23.99	15.26	40.4	0.54	0.05	0.86	0.2	0.8
MgO	1.8	1.28	3.09–31.2	1.54	5.41	4.27	0.00	–	–	0.06	0.05
MnO	0.8	12.97	0.63–2.67	6.91	0.19	0.25	0.00	–	–	–	–
CaO	21.4	26.55	0.33–4.35	23.98	22.45	1.59	6.38	0.05	1.79	18.52	12.09
PbO	0.2	0.28	0.02–0.07	0.25	–	–	2.83	–	–	–	–
ZnO	8.3	1.29	0.01–2.82.	4.78	0.09	–	0.10	–	–	–	0.16
Cr_2O_3	0.1	–	–	–	0.06	0.05	–	–	–	–	–
BaO	0.3	–	–	–	–	–	4.04	0.28	5.92	0.17	–
Na_2O	0.7	–	–	–	0.08	0.23	0.54	0.88	1	0.5	3.51
K_2O	0.9	–	–	–	–	0.8	8.53	13.94	9.23	0.22	0.35
References	A	B	B and C	B	C	C	B	C	C	C	C

Ano Anorthite, *Clif* Clinoferrosilite, *Kir* Kirschsteinite, *He* Hedenbergite, *Leu* Leucite, *Wo* Wollastonite, *Me* Melilite, *Mg* Magnetite, *Ol* Olivine, *Gl* Glass, *Py* Pyroxene, K fel-K-feldspar, *Hya* Hyalophane, *La* Labradorite

A: Deneele (2002), *B*: Puziewicz et al. (2007), *C*: Piatak and Seal (2010)

Table 5.7 Microprobe studies of each mineral phase present in Zn slags

	Melilite group			Silicates			Oxides	
				Al–Si–O (other silicates)				
Minerals (% wt)	Me	Ha	Wil	Mul	Al_2SiO_5	Pb-Si	ZnCr	Gah
SiO_2	34.14	39.63	29.86	22.38	35.06	27.78	0.03	0.08
TiO_2	0.05	–	0.00	0.84	0.56	4.51	0.08	0.25
Al_2O_3	0.80	1.75	0.03	72.89	59.38	10.60	1.96	50.72
FeO and Fe_2O_3	2.03	0.98	0.18–1.16	2.55	2.4	8.44	14.65	10.52
MgO	3.90	0.34	0.05–0.23	0.04		4.29	0.97	3.19
MnO	0.17	–	10.77	–	0.17	–	2.27	0.19
CaO	27.20	33.26	0.00	–	0.25	–	–	–
PbO	17.86	–	0.04	–		28.92	0.24	0.13
ZnO	13.16	22.61	58.32–69.66	–		1.42	18.14	31.08
Cr_2O_3	–	–	–	–		–	61.13	4.03
BaO	–	0.38	–	–		8.96	–	–
Na_2O	–	–	–	–	0.33	0.20	–	–
K_2O	–	0.04	–	–	0.68	1.82	–	–
References	B	C	B and C	C	C	B	A	A

Me Melilite, *Ha* Hardystonite, *Wil* Willemite, *Mul* Mullite, *Spl* Spinels, *Pb* Si - Lead silicate, *ZnCr* Zincochromite, and *Gah* gahnite
A: Deneele (2002), *B*: Puziewicz et al. (2007), *C*: Piatak and Seal (2010)

across the slag samples. Franklinite, magnesiochromite and magnetite are dominant spinel minerals found in Pb slags where the concentration of Zn varies from 8.92 to 19.91% in weight (Table 5.5). On the other hand, zincochromite and gahnite are found in Zn slags where the Zn content can be 18–31% in weight (Table 5.7).

The glassy matrix can be heterogeneous with the oxide proportions varying significantly for both Pb and Zn slags where the composition can be described in terms of SiO_2, CaO, total Fe ($FeO + Fe_2O_3$), Al_2O_3, ZnO and PbO. A relative viscosity of the melt simply relies on the ratio of ($CaO + FeO + MgO + MnO + K_2O + Na_2O$) / ($SiO_2 + Al_2O_3$) in % weight (Manasse et al. 2001). Si is the main cation forming silicate network, whereas Al and Fe(III) are not only involved in network formation, but also in network modification. Only if Al is charge balanced with other cations such as K, Na or Ca, it can be considered as a network former.

5.3 Weathering of Slags

Unlike ferrous slags (Fe industries), non-ferrous slags from base metal smelters are composed of potentially toxic elements (e.g. As, Cd, Cu, Pb, Zn) and can lead to the contamination of surface and ground water (Parsons et al. 2001). Thus, many studies have contributed to the understanding of the stability of slags and their short and long term leaching behavior by simulating either chemically or biologically influenced weathering experiments.

5.3.1 Chemically Induced Weathering

5.3.1.1 Leaching Assessment of Slags

Several leaching tests have been extensively performed by various researchers to assess the stability of slags, the leaching behaviour of metals in terms of short-protocol leaching tests (Table 5.8) as well as long-term leaching tests by prolonging slag-water interaction time (Table 5.9). These studies focus on slags and smelter related samples (Pb slags, Zn slags, Pb-Cu slags, Cu-Zn slags, secondary Pb slags, fly ash of secondary Pb smelters) as well as many environmental conditions (pH, liquid-to-solid ratios, various leachant, agitation speed, oxic/anoxic conditions, and contact time).

Details of most common protocol tests applied to metallurgical slags are given in Table 5.8. Each test is different, based on different environmental simulations: the special waste extraction procedure (SWEP) developed by British Columbia intended only for metallurgical and mineral wastes; the diffusion-leaching NEN 7341 test developed in the Netherlands to simulate the successive pH drop from neutral to acidic conditions; the EN 12457–2 test developed by the European Union to simulate normal rainfall conditions; the synthetic precipitation leach procedure (SPLP) as developed by the American National Mining Association to simulate acid rain; the standard toxicity characterisation leaching procedure (TCLP) test developed by the USEPA to simulate the co-disposal scenario with municipal solid waste; and leaching assessment to test the reuse potential of Zn slags in cement.

Likewise, details of many long-term leaching assessment tests applied to metallurgical slags are given in Table 5.9. These studies at laboratory-batch-scale level cover equilibrium leaching tests under saturated conditions; intermittent or continuous leachant renewal conditions (Barna et al. 2004), kinetic leaching test (Ettler et al. 2008), pH-dependent leaching test (De Andrade Lima and Bernardez 2013; Ganne et al. 2006; Vítková et al. 2013), simulation of weathering in the soil environment (Ettler et al. 2005a; Ettler and Johan 2014) and remobilisation of contaminated sediments (Vdovic et al. 2006). In addition, many studies have been done at pilot scale or field level: column leaching tests as well as outdoor weathering of slag dumps (Seignez et al. 2006, 2007, 2008), field leaching experiments (Piatak et al. 2004), and the establishment of a relationship between laboratory-based test results and measured water compositions at a real site (Parsons et al. 2001).

Results of dynamic leaching assessment tests have been combined with several geochemical computer models such as PHREEQC-2 (Ettler et al. 2004, 2005a; 2008, 2009; Navarro et al. 2008), Minteq A2 (Ettler et al. 2005a; Ganne et al. 2006), Minteq A4 (Vítková et al. 2013) or more sophisticated geochemical codes such as

Table 5.8 Protocol tests for short-term leaching assessment of slags

Name	Sample	Experimental conditions					References
		pH	L/S ratio (ml/g)	Leachant types (per l)	Shaking (rpm)	Duration	
British Columbia special waste extraction procedure (SWEP)	Pb slags	5	20	Acetic acid	10	24 hrs	A
Dutch diffusion-leaching test, NEN 7341	Zn slag	7 and 4	50	1 M HNO_3	–	6 hrs	B
European norm EN 12457–2 (EN)	Fly ash of secondary Pb smelter	5.75	20	MiliQ + deionized water	10	24 hrs	C
	Pb–cu blast furnace slags						D
	Zn and Pb slags						E, F
Leaching assessment	Zn slag in cement	9.7	4	Deionised water	–	24 hrs	G
		13.4		Buffer solution			
		11.8		Saturated (CaO) solution			
Synthetic precipitation leaching procedure (SPLP)	Secondary Pb slag	4.2	20	Deionised water + H_2SO_4+ HNO_3	30	18 hrs	H
	Zn and Pb slags						A, I, J
Toxicity characteristic leaching procedure (TCLP)	Secondary Pb slag	4.93	20	5.7 ml acetic acid +500 ml MiliQ +64.3 ml of 1 M NaOH	30	18 hrs	H
	Cu-Zn slag						I
	Fly ash of secondary Pb smelters						C
	Pb–Cu blast furnace slags						D
	Pb and Zn slag						A, F

A: de Andrade Lima and Bernardez (2011, 2013), *B*: Ganne et al. (2006), *C*: Ettler et al. (2005b), *D*: Ettler et al. (2009), *E*: Saikia et al. (2008, 2012), *F*: Yin et al. (2014), *G*: Morrison et al. (2003), *H*: Lewis and Hugo (2000), *I*: Parsons et al. (2001), *J*: (Piatak et al. 2004, 2010)

Table 5.9 Assessment tests for long-term heavy metal mobility from slags

			Experimental conditions					
Name (if any)	Objectives	Samples	pH	L/S ratio (ml/g)	Leachant types (per l)	Shaking (rpm)	Duration	Reference
pH_{stat} leaching test	Leaching behaviour as a function of pH	Pb, Zn slags and fly ash	5–12	10	HNO_3, HCl and NaOH	–	7 days	A, B, C
Remobilisation experiments	(i) slag vs. sediment in river water, (ii) sediment + slag in river water	Pb, Zn slags, and polluted sediments	8.27–8.7	–	River water with 7.8–9.5 mg/dm^3 vs 1.8–3.2 mg/dm^3 of O_2	–	2–10 days	D
Kinetic leaching test	Solubility-controlling mechanisms	Fly ash of secondary Pb smelters	7	10	Demineralised water	60	30 days	E
Weathering in soil environments	Effect of low molecular weight organic acids	Pb slags	2.4	10	20 and 8 mM citric acid solutions	–	30 days	F
	Effect of high molecular weight organic acids		3.68	10	Fulvic acid and peat water (DOC: 50 vs 47 mg/L)	60	112 days	G
Column leaching test for phytostabilisation	Long-term behavior and mobility of metal	Slag dump	–	–	Deionised water	–	17, 25, 30, 55 days	H
Column leaching test	Structure and composition on metal mobility	Pb slags (grain vs. polished section)	5.6	10	Pure water (60 ml/h recirculation flow rate)	–	15, 26 days	I
Outdoor weathering test	Natural weathering of slag heap		–					

Saturated leaching tests on monolithic material	Contaminants release rate and mass transfer rate	Road materials containing Pb and Zn slags	13	2 ml/cm^2	Demineralised and synthetic pore water (1 g ca $(OH)_2$ + 2.2 g NaOH +1.6 g KOH)		5–6 months	J
Lab/pilot-scale: Intermittent wetting conditions	By varying humidity, temperature, atmospheric CO_2					–	8–16 months	
Normalised static leaching procedures (AFNOR)	Long-term assessment	Pb-Zn slags	2, 5.6	10	MiliQ + DI + HNO_3, vs pure DI	60	12 months	K

A: Ganne et al. (2006), *B*: de Andrade Lima and Bernardez (2013), *C*: Vítková et al. (2013), *D*: Vdovic et al. (2006), *E*: Ettler et al. (2008), *F*: Ettler et al. (2004), *G*: Ettler et al. (2005a), *H*: Lewis and Hugo (2000), *I*: Seignez et al. (2006, 2007, 2008), *J*: Barna et al. (2004), *K*: Ettler et al. (2003), Morrison et al. (2003).

WHAM (Model VI) or ECOSAT (NICA-Donnan model) for accurate prediction of the metal complexation by dissolved organic matter (Ettler et al. 2005a).

5.3.1.2 Applicability of Leaching Tests to Metallurgical Slags

The significant differences between both short-protocols and long-term leaching tests are the contact time, type of leachant, agitation rate, pH, liquid to solid (L/S) ratios, and particle size of the sample. All protocol assessment tests are batch tests, quick and simple to carry out with reproducible results. As they are intended for short-term risk assessment and characterisation of slags at a glance, a combination of these tests can give an idea of the leaching behavior of metals under different leaching scenarios (i.e., landfill, acid rain or soil dumping). However, the requirement for particle size reduction of the slags during these tests does not reflect the conditions in which metallurgical slags are generally processed or disposed of. They are usually rocklike, monolithic structures, where leaching is minimized.

Lewis and Hugo (2000) pointed out that the application of TCLP to mineral processing and metallurgical wastes has been challenged because of the high acid neutralising capacity (ANC) of the slags, rendering true assessment of the leaching potential impractical. Each leaching test protocol is different, based on the different environmental simulations and purposes, nature of targeted wastes or slags, nature of leachant used, different duration of each test, and the origin of the country where it is developed reflecting its country's regulations and standards. The application of two or more tests (TCLP + SPLP + SWEP) to one single slag can overcome such controversy and might thus be beneficial for short-term assessment. Short-term assessment is quick, simple to carry out and provides reproducible results, and a combination of these tests can even be beneficial in assessing the environmental impact of slags in different weathering conditions.

Piatak et al. (2015) pointed out that many results from leaching tests are not consistent as potentially toxic trace elements are present among various phases whose relative reactivity and leachability can be the key to understanding the stability of slags. Partitioning of Zn can be related to the overall bulk Zn concentration: Zn was hosted mainly in spinel and silicate phases in Zn rich samples, whereas it was mainly present in sulphides in lower-bulk Zn concentrations (Piatak et al. 2015).

On the other hand, the long term leaching tests cover more criteria. As size reduction is not the requirement, they represent conditions closer to the field. They also consider whether or not the acid-base neutralising capacity of the slag will be depleted over longer periods of contact time. In addition, the flow conditions of the water (downward and horizontal flow) along with the simulation of rainfall (intermittent and cyclic wetting of the slag) are the main advantages of long-term leaching tests over short-term ones. The applicability can be challenging if only one test is applied and the amount of metals leached out can be either under or overestimated. Thus, the application of both short and long-term leaching assessment tests should be considered to fully understand the leaching behavior of the metallurgical slags.

5.3.1.3 Chemical Weathering Mechanisms

Both Ettler et al. (2003) and Mahé-Le Carlier et al. (2000) observed that the alteration of Pb-Zn slags is initiated by the leaching of network modifier elements like Ca, Mg, Mn and Fe. Curtis (2003) further explained that it is due to the hydrolysis reaction and the nucleophilic property of water on the silicon atom (Eq. 5.1):

$$\equiv Si - O - M + H^{+} + OH^{-} \rightleftharpoons \equiv Si - O - H^{+} + (MOH\ or\ OH^{-}) + M^{+} \quad (5.1)$$

Conradt (2008) pointed out the three different equilibria during the slag alteration: (1) an electrochemical equilibrium at the slag surface, (2) a new thermodynamic equilibrium within aqueous solution owing to element dissolution, and (3) the equilibrium which involves the solubility formation of stoichiometric hydrates of hydroxide phases due to hydrolysis.

With increasing hydration energy, H–O–H bonds are eventually broken with loss of protons (H^+ ions) during an exchange with cations (Curtis 2003). The exchange reaction between H^+ ions and cations from the slags leads to an increase of the pH, creating a neutral to moderately basic environment. This accelerates the silica release phenomenon by a probable mechanism of breaking strong links of the residual glass by the hydroxyl ions of the solution. The condensation reaction between two silanol groups leads to the formation of hydrated silica gel (Eq. 5.2):

$$\equiv Si - O - H^{+} + \equiv Si - O - H^{+} \rightleftharpoons \equiv Si - O - Si \equiv + \ H_2O \quad (5.2)$$

The newly formed silica gel or secondary phases serve as the protection layer on the surface of altered slag, thus limiting the contact between the slag and the solution, which consequently leads to the pore-diffusion control of the aqueous solution through this growing layer (Conradt 2008). Many silicates and non-silicate phases in the slags are observed to release metals into solution at different rates. The dissolution rates of several silicates and oxides are pH-dependent, depicting a U-shaped curve when dissolution is plotted against pH on a log scale during steady, but far-from-equilibrium dissolution (Brantley et al. 2008). The overall dissolution rate of the slag can be the sum of the rates of the individual silicate and oxide phases. The newly formed silica gel or secondary phases on the slag surface which is adjacent to the solution can also be key to control the overall dissolution rate of the slag, i.e. the solid/liquid interaction affects the rate more than the in-depth leached layers (Hamilton et al. 2001).

5.3.2 Biologically Induced Weathering

In contrast to the extensive studies on chemical alteration of slags, only a few studies have focused on the involvement of microbial activity in slags alteration. To fully describe the state of knowledge on the topic and better highlight the great potential of bioleaching for metal recovery from metallurgical slags, this section will be extended to the dissolution of single glass or silicate phases in the presence of bacteria, and the interaction of bacteria and heavy metals, rather than be limited just to the bio-alteration of lead and zinc metallurgical slags.

Microorganisms are well known for their participation in mineral formation and dissolution. Some microorganisms are able to (1) oxidize or reduce many dissolved inorganic species, (2) detoxify toxic ones, and (3) actively or passively take up one or many of them which are later converted into their cellular structure. Other microorganisms are able to utilize minerals as they are not only a reservoir of many trace elements but also of electron acceptors, thus, providing energy by respiration (Ehrlich 1996). Many bacterial strains from different genera have shown their ability to weather several minerals (Uroz et al. 2009). They can destabilise and dissolve a mineral either as a single strain or in association with other microbial species.

5.3.2.1 Bioleaching of Slags

Bio-weathering due to heterotrophic microorganisms is focused here, owing to the high acid-buffering capacity and alkaline nature of Pb/Zn metallurgical slags, and to the fact that these slags are dumped in soil where organic matter and nutrients are present and can, therefore, be used by heterotrophic microorganisms. There is a growing interest in the application of heterotrophic leaching of alkaline slags and filter dusts/oxides from metal processing, as most *Thiobacilli* cannot effectively solubilise alkaline wastes with pH values above 5.5 (Gadd 2000). Eleven heterotrophic microorganisms from an alkaline slag dump have been isolated, including nine bacterial strains, one fungus and one yeast isolate (Willscher and Bosecker 2003). In addition, the K-feldspar dissolution was enhanced in the presence of heterotrophic bacteria, where the degree of dissolution depended on the different bacterial strains and growth conditions applied: *Serratia marcescens* was very effective in enhancing feldspar dissolution (Hutchens et al. 2003). The influence of bacteria *(Azotobacter chroococcum, Bacillus megaterium* and *Bacillus mucilaginosus*) on Pb and Zn speciation, mobility and bioavailability in soil have been described in a series of single chemical extraction, sequential extraction and *in situ* soil solution extraction technologies (Wu et al. 2006). Heterotrophic microorganisms (*Microbacterium sp., Promicromonospora sp. and Pseudomonas cedrina)* solubilise many metals from minerals via oxidation as well as by secreting complexing agents (Willscher et al. 2007).

5.3.2.2 Sorption/Complexation of Metals by Bacterial Cells, EPS, Siderophores

During the alteration of basaltic glass and a vitrified bottom ash, the sorption of many dissolved elements (Si, Mg, Fe, Ti, Ba, Co, Zn, Cu, Ni and Cr) was found in the biofilm and adsorbed onto *P. aeruginosa* cells (Aouad et al. 2006). The three conceptual reactive sites are acidic (carboxyl and/or phosphodiester), neutral (phosphomonoester) and basic (amine and/or hydroxyl) groups. Three bacteria (*Cupriavidus metallidurans CH34, Pseudomonas putida ATCC12633,* and *Escherichia coli K12DH5R*) were further investigated for Zn sorption (Guine et al. 2006). The increasing Fe concentration observed was due to the production of pyoverdine and its chelation capacities (Aouad et al. 2006; Yin et al. 2014). Moreover, the production of chelating compounds (exopolymers, siderophores and pigments) was highlighted by Hutchens et al. (2003) as a possible mechanism behind enhanced K-feldspar dissolution.

Extracellular polymeric substances (EPS) secreted from bacteria also play an important role in binding with metal cations due to their anionic properties. Pb has a greater affinity for EPS than Cd where the mineral fraction of the EPS is probably involved to a large extent in the sorption and binding strength between metals and EPS (Guibaud et al. 2006). Similarly, the binding affinity of EPS from fungi (*Pestalotiopsis sp.*) for Pb is higher than for Zn (Moon et al. 2006). In addition, the pH plays an important role in metal sorption onto EPS: no or minimum sorption occurs at acidic pH and the percentage of metal adsorption increases with higher pH (Guibaud et al. 2006).

5.3.2.3 Sorption/Bio-weathering Mechanisms

The possible bio-alteration mechanism along with different biochemical interactions between the heterotrophic bacterium *Pseudomonas aeruginosa* and Pb slag (LBF) is illustrated in Fig. 5.2 Chemical alteration of slag induces solid-liquid reactions with the hydrolysis of Si^{4+} and dissolution of network modifying elements like Ca^{2+} and Mg^{2+}. The matrix neutralisation reactions between cations and H^+ from the liquid medium lead to the accumulation of OH^- ions, which results in a pH rise. Under the bio-alteration of slags, Fe dissolution could be significantly enhanced by the siderophores and bacteria cells serve as bio-sorbent owing to their higher surface to volume ratio (Konhauser 2007). Depending on the moiety donating oxygen ligands for Fe^{3+} coordination, siderophores are grouped into three types: (i) catecholates or phenolates, (ii) hydroxamates or carboxylates, (iii) α-hydroxy-carboxylic groups and (iv) a mixture of these groups (Saha et al.

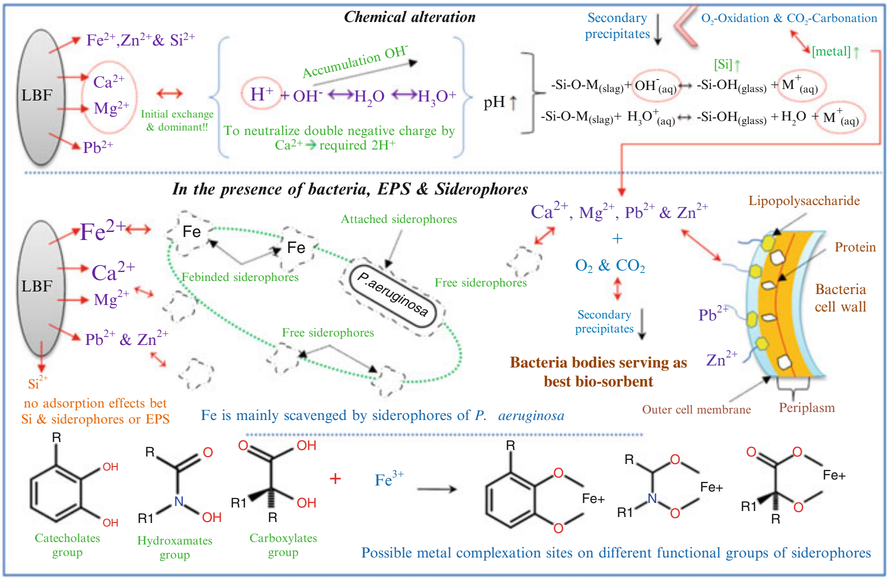

Fig. 5.2 Alteration of Pb slag by the heterotrophic bacterium *Pseudomonas aeruginosa* (Modified from van Hullebusch et al. 2015)

2013), where complexation occurs not only with Fe, but also with other metals like Cu and Zn (Potysz et al. 2016).

5.3.3 Mineralogical Control on Metal Bioleachability

The primary mineral phases present in Pb and Zn slags (Tables 5.3 and 5.4) control the release of metals and metalloids into the environment under weathering conditions. The slag glass phase is more reactive and liberates minor relic sulfide ores, or metallic droplets entrapped in it (Ettler et al. 2003; Parsons et al. 2001). Zinc is probably leached either from sulfide/metallic droplets such as Fe-rich wurtzite ((Fe + Zn)S), or from Zn-bearing silicates (*e.g.* melilite) and glass. Spinels, main Zn concentrators, as well as willemite (Zn_2SiO_4), are most resistant to weathering and do not significantly contribute to Zn liberation (Ettler et al. 2003). On the other hand, Zn partitioned volumetrically into minor sulphides is prone to weathering and liberation of Zn (Piatak and Seal 2010). Other phases such as franklinite are not very reactive and are stable up to pH 2 (Ganne et al. 2006). Moreover, the formation of secondary precipitates such as amorphous hydrous ferric oxides (HFO) and aluminum oxyhydroxide (AlOOH) are also controlling the release and mobility of metal and metalloids through sorption and/or co-precipitation (Ettler et al. 2009).

More studies have been done on the bio-accessibility of Pb and Zn in soils from mining and smelter areas (Ettler et al. 2012), from slags (Bosso and Enzweiler 2008) and the Pb mineralogy control on leaching and relative bio-accessibility (Romero et al. 2008). Glass phases are very important in controlling heavy metal mobility as well as bio-accessibility when being ingested, while the heavy metals in a silicate matrix are protected against leaching. The presence of heterotrophic bacteria enhances the dissolution of minerals as olivine (clinochlore, lizardite, nimite and willemseite) was significantly reduced in quantity (Chiang et al. 2013). Similarly, the presence of *Pseudomonas aeruginosa* dramatically enhances the solubility, and therefore the mobility of metals contained in Pb slags, lead blast furnace (LBF) slags (van Hullebusch et al. 2015; Yin et al. 2014).

5.3.4 Secondary Bioprecipitates

Geochemical models are used to predict the species of many dissolved elements, to calculate the saturation indices of these species and to predict the formation of possible solid phases controlling the leachate composition (Piatak et al. 2004). Models such as PHREEQC-2 (Ettler et al. 2004, 2005a, 2008, 2009; Navarro et al. 2008), Minteq A2 (Ettler et al. 2005a; Ganne et al. 2006), Minteq A4 (Vítková et al. 2013), Visual MINTEQ version 3.0 (Yin et al. 2016) as well as more sophisticated geochemical codes such as WHAM (Model VI) or ECOSAT (NICA-Donnan model) were used for accurate prediction of the metal complexation by dissolved organic matter (Ettler et al. 2005a).

These models predict the possible secondary precipitation formation by calculating the saturation index (SI), as follows (Eq. 5.3):

$$SI = \log\left(\frac{Q}{K}\right) \tag{5.3}$$

where Q is the ion activity product and K the equilibrium constant for the dissolution reaction. If the SI is zero, it reflects equilibrium, negative values indicate under-saturation and a positive values indicate super-saturation, thus indicating the formation of possible secondary precipitates (Parsons et al. 2001).

Under oxidizing conditions, with a supply of atmospheric CO_2 at pH 6–9, formation of cerussite ($PbCO_3$) and amorphous hydrous ferric oxides (HFO) has been reported reflecting the *long-term leaching assessment conditions* (Ettler et al. 2003). Precipitation of HFO is mainly controlled by major dissolution of mainly Fe-bearing phases releasing Fe^{2+} into the solution with the contribution of other minerals (silicates, oxides and glass), and the time required for oxidation of Fe^{2+} to Fe^{3+} (Ettler et al. 2005a). In case of *soil weathering environments* with the presence of low or high molecular weight organic acids, the formation of well-developed calcite ($CaCO_3$) crystals and an amorphous organo-mineral matrix of HFO and amorphous SiO_2 was reported (Ettler et al. 2004). Metals like Pb, Zn, Cu and As present in the leachate were subsequently adsorbed onto newly formed HFO or trapped within the calcite structure. Zn exhibits a more pronounced mobility and is adsorbed on HFO/FO only at pH values higher than 7 (Ettler et al. 2005a). Similar adsorption of Pb onto HFO was also found *after natural alteration* of metallurgical slags from old dump sites (Mahé-Le Carlier et al. 2000).

In addition to HFO, AlO(OH) and phases such as chalcanthite ($CuSO_4.5H_2O$), siderotil ($Fe^{2+}CuSO_4.5H_2O$), jarosite ($KFe^{3+}{}_3(OH)_6(SO_4)_2$), brochantite ($Cu_4SO_4(OH)_6$) and gypsum ($CaSO_4.2H_2O$) were reported at old base-smelter slag dump sites undergoing natural weathering (Piatak et al. 2004). Moreover, brianyoungite [$Zn_3(CO_3,SO_4)(OH)_4$], and less common phases like bechererite [$(Zn,Cu)_6Zn_2(OH)_{13}[(S,Si)(O,OH)_4]_2$] were identified as a secondary coating and as fibrous/ bladed crystals filling in cavities of zinc slags on dump sites (Piatak and Seal 2010). Chiang et al. (2013) reported that the alkaline bioleaching of alkaline slags materials took place when solubilisation of primary minerals and precipitation of secondary minerals simultaneously occur. The alteration of primary minerals such as dicalcium-silicate, bredigite and periclase, and the formation of new secondary phases such as merwinite and calcite was reported.

5.4 Conclusion

Comprehensive and extensive studies have been established concerning chemical alteration of slags under different experimental conditions. These studies indicate that detailed characterization of slag mineralogy, surface area, and dissolution of slags and mobility of metals is required, as well as the application of at least two or even three simple leaching tests (TCLP + SPLP + SWEP). This might be beneficial for short-term risk assessment, as these tests provide reproducible results and their combination can be beneficial in assessing the environmental impact of slags in different weathering conditions. However, most studies have been restricted to laboratory-based leaching assessments only. Thus, many questions remain concerning field weathering conditions in order to predict the long-term (i.e. 10–100 of years) reactivity of these metallurgical wastes (Ettler and Johan 2014) or to relate laboratory test results with measured values in the field. In addition, it is still difficult to determine the alteration yields and kinetics of each individual crystalline or glassy phase present in metallurgical slags contributing to the overall alteration of slags even at the laboratory scale.

Compared to chemical alteration studies of metallurgical slags, the focus on the involvement of microbial activity in natural alteration of these slags is relatively poor. Further research is required to investigate the microorganisms involved in the leaching of alkaline slag dumps and to pinpoint the physiological processes involved in metal solubilisation. With such knowledge, heterotrophic leaching can be an alternative for bio-metal recovery from alkaline slags where improvement in the leaching performance can be achieved by manipulation of the leaching conditions.

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References

Aouad G, Crovisier JL, Geoffroy VA, Meyer JM, Stille P (2006) Microbially-mediated glass dissolution and sorption of metals by *Pseudomonas aeruginosa* cells and biofilm. J Hazard Mater 136:889–895. doi:10.1016/j.jhazmat.2006.01.026

Audry S, Schafer J, Blanc G, Jouanneau JM (2004) Fifty-year sedimentary record of heavy metal pollution (Cd, Zn, Cu, Pb) in the lot river reservoirs (France). Environ Pollut 132:413–426. doi:10.1016/j.envpol.2004.05.025

Barna R, Moszkowicz P, Gervais C (2004) Leaching assessment of road materials containing primary lead and zinc slags. Waste Manag 24:945–955. doi:10.1016/j.wasman.2004.07.014

Bosso ST, Enzweiler J (2008) Bioaccessible lead in soils, slag, and mine wastes from an abandoned mining district in Brazil. Environ Geochem Health 30:219–229. doi:10.1007/s10653-007-9110-4

Brantley SL, Kubicki JD, White AF (2008) Kinetics of water-rock interaction. Spring, Berlin, pp 1–843. doi:10.1007/978-0- 387-73563-4

Chiang YW, Santos RM, Monballiu A, Ghyselbrecht K, Martens JA, Mattos MLT, Gerven TV, Meesschaert B (2013) Effects of bioleaching on the chemical, mineralogical and morphological properties of natural and waste-derived alkaline materials. Miner Eng 48:116–125. doi:10.1016/j.mineng.2012.09.004

Conradt R (2008) Chemical durability of oxide glasses in aqueous solutions: a review. J Am Ceram Soc 91:728–735. doi:10.1111/j.1551-2916.2007.02101.x

Curtis CD (2003) The aqueous geochemistry of metals in the weathering environment: strengths and weaknesses in our understanding of speciation and process. Mineral Mag 67:235–246. doi:10.1180/0026461036720097

De Andrade Lima LRP, Bernardez LA (2011) Isotope source signatures for a primary lead smelter located close to Todos Os Santos bay, Brazil. Soil Sediment Contam: An Int J 20:672–687. doi:10.1080/15320383.2011.594109

De Andrade Lima LRP, Bernardez LA (2013) Evaluation of the chemical stability of a landfilled primary lead smelting slag. Environ Earth Sci 68:1033–1040. doi:10.1007/s12665-012-1805-x

Deneele D (2002) Caracterisation, simulations experimentales et thermodynamiques de l'alteration de dechets vitreux: les scories de première fusion de plomb et de zinc. PhD thesis Université de Lille I, France, pp 1–242

Douay F, Roussel H, Pruvot C, Loriette A, Fourrier H (2008) Assessment of a remediation technique using the replacement of contaminated soils in kitchen gardens nearby a former lead smelter in northern France. Sci Total Environ 401:29–38. doi:10.1016/j.scitotenv.2008.03.025

Douay F, Pruvot C, Waterlot C, Fritsch C, Fourrier H, Loriette A, Bidar G, Grand C, De Vaufleury A, Scheifler R (2009) Contamination of woody habitat soils around a former lead smelter in the north of France. Sci Total Environ 407:5564–5577. doi:10.1016/j.scitotenv.2009.06.015

Ehrlich HL (1996) How microbes influence mineral growth and dissolution. Chem Geol 132:5–9. doi:10.1016/S0009-2541(96)00035-6

Ettler V, Johan Z (2003) Mineralogy of metallic phases in sulphide mattes from primary lead smelting. Com Rend Geosci 335:1005–1012. doi:10.1016/j.crte.2003.09.005

Ettler V, Johan Z (2014) 12 years of leaching of contaminants from pb smelter slags: geochemical/mineralogical controls and slag recycling potential. Appl Geochem 40:97–103. doi:10.1016/j.apgeochem.2013.11.001

Ettler V, Johan Z, Touray JC, Jelínek E (2000) Zn partitioning between glass and silicates phases in historical and modern lead-zinc slags, Czech Republic. Earth Planet Sci 331:245–250. doi:10.1016/S1251-8050(00)01416-6

Ettler V, Legendre O, Bodenan F, Touray JC (2001) Primary phases and natural weathering of old lead–zinc pyrometallurgical slag from Príbram, Czech Republic. Can Mineral 39:873–888. doi:10.2113/gscanmin.39.3.873

Ettler V, Piantone P, Touray JC (2003) Mineralogical control on inorganic contaminant mobility in leachate from lead-zinc metallurgical slag: experimental approach and long-term assessment. Mineral Mag 67:1269–1283. doi:10.1180/0026461036760164

Ettler V, Komarkova M, Jehlicka J, Coufal P, Hradil D, Machovic V, Delorme F (2004) Leaching of lead metallurgical slag in citric solutions-implications for disposal and weathering in soil environments. Chemosphere 57:567–577. doi:10.1016/j.chemosphere.2004.07.022

Ettler V, Jehlicka J, Masek V, Hruska J (2005a) Leaching behaviour of lead metallurgical slag in high-molecular-weight (HMW) organic solutions. Mineral Mag 69:737–747. doi:10.1180/0026461056950284

Ettler V, Mihaljevic M, Sebek O, Strnad L (2005b) Leaching of APC residues from secondary Pb metallurgy using single extraction tests: the mineralogical and the geochemical approach. J Hazard Mater 121:149–157. doi:10.1016/j.jhazmat.2005.02.001

Ettler V, Sebek O, Grygar T, Klementova M, Bezdička P, Slavikova H (2008) Controls on metal leaching from secondary Pb smelter air pollution control residues. Environ Sci Technol 42:7878–7884. doi:10.1021/es801246c

Ettler V, Johan Z, Kříbek B, Šebek O, Mihaljevič M (2009) Mineralogy and environmental stability of slags from the Tsumeb smelter, Namibia. Appl Geochem 24:1–15. doi:10.1016/j.apgeochem.2008.10.003

Ettler V, Kříbek B, Majer V, Knésl I, Mihaljevič M (2012) Differences in the bioaccessibility of metals/metalloids in soils from mining and smelting areas (Copperbelt, Zambia). J Geochem Explor 113:68–75. doi:10.1016/j.gexplo.2011.08.001

Gadd GM (2000) Bioremedial potential of microbial mechanisms ofmetal mobilisation and immobilisation. Environ Biotech:271–279. doi:10.1016/S0958-1669(00)00095-1

Ganne P, Cappuyns V, Vervoort A, Buve L, Swennen R (2006) Leachability of heavy metals and arsenic from slags of metal extraction industry at Angleur (Eastern Belgium). Sci Total Environ 356:69–85. doi:10.1016/j.scitotenv.2005.03.022

Guibaud G, van Hullebusch E, Bordas F (2006) Lead and cadmium biosorption by extracellular polymeric substances (EPS) extracted from activated sludges: pH-sorption edge tests and mathematical equilibrium modelling. Chemosphere 64:1955–1962. doi:10.1016/j.chemosphere.2006.01.012

Guine V, Spadini L, Sarret G, Muris M, Delolme C, Gaudet JP, Martins JMF (2006) Zinc sorption to three gram-negative bacteria combined titration, modeling, and EXAFS study. Environ Sci Technol 40:1806–1813. doi:10.1021/es050981l

Hamilton JP, Brantley SL, Pantano CG, Criscenti LJ, Kubicki JD (2001) Dissolution of nepheline, jadeite and albite glasses toward better models for aluminosilicate dissolution. Geochim Cosmochim Acta 65:3683–3702. doi:10.1016/S0016-7037(01)00724-4

Hudson-Edwards KA, Jamieson HE, Lottermoser BG (2011) Mine wastes: past, present, future. Elements 7:375–380. doi:10.2113/gselements.7.6.375

Hutchens E, Valsami-Jones E, Mceldowney S, Gaze W, Mclean J (2003) The role of heterotrophic bacteria in feldspar dissolution–an experimental approach. Mineral Mag 67:1157–1170. doi:10.1180/0026461036760155

Konhauser KO (2007) Introduction to geomicrobiology. Blackwell publishing, Hoboken

Lewis AE, Hugo A (2000) Characterisation and batch testing of a secondary lead slag. J South Afr Inst Min Metall**,** 365–370. doi: v100n06p365

Lottermoser BG (2002) Mobilisation of heavy metals from historical smelting slag dumps, North Queensland, Australia. Mineral Mag 66:475–490. doi:10.1180/0026461026640043

Mahé-Le Carlier C, Le Carlier De Veslud C, Ploquin A, Royer JJ (2000) L'altération naturelle des scories de la métallurgie ancienne: un analogue de déchets vitrifiés. Earth Planet Sci 330:179–184. doi:10.1016/S1251-8050(00)88666-8

Manasse A, Mellini M, Viti C (2001) The copper slags of the Capattoli valley, Campiglia Marittima, Italy. Eur J Mineral 13:949–960. doi:10.1127/0935-1221/2001/0013/0949

Moon SH, Park CS, Kim YJ, Park YI (2006) Biosorption isotherms of Pb (II) and Zn (II) on Pestan, an extracellular polysaccharide, of *Pestalotiopsis Sp.* Kctc 8637p. Process Biochem 41:312–316. doi:10.1016/j.procbio.2005.07.013

Morrison C, Hooper R, Lardner K (2003) The use of ferro-silicate slag from ISF zinc production as a sand replacement in concrete. Cem Concr Res 33:2085–2089. doi:10.1016/S0008-8846(03)00234-5

Navarro A, Cardellach E, Mendoza JL, Corbella M, Domènech LM (2008) Metal mobilisation from base-metal smelting slag dumps in sierra Almagrera (Almería, Spain). Appl Geochem 23:895–913. doi:10.1016/j.apgeochem.2007.07.012

Nickel EH (1995) Definition of a mineral. Eur J Mineral 7:1213–1215. doi:10.1127/ejm/7/5/1213

Parsons MB, Bird DK, Einaudi MT, Alpers CN (2001) Geochemical and mineralogical controls on trace element release from the base-metal slag dump, California. Appl Geochem 16:1567–1593. doi:10.1016/S0883-2927(01)00032-4

Pelfrene A, Waterlot C, Mazzuca M, Nisse C, Bidar G, Douay F (2011) Assessing cd, pb, zn human bioaccessibility in smelter-contaminated agricultural topsoils (Northern France). Environ Geochem Health 33:477–493. doi:10.1007/s10653-010-9365-z

Piatak NM, Seal RR (2010) Mineralogy and the release of trace elements from slag from the Hegeler zinc smelter, Illinois (USA). Appl Geochem 25:302–320. doi:10.1016/j.apgeochem.2009.12.001

Piatak NM, Seal RR, Hammarstrom JM (2004) Mineralogical and geochemical controls on the release of trace elements from slag produced by base- and precious-metal smelting at abandoned mine sites. Appl Geochem 19:1039–1064. doi:10.1016/j.apgeochem.2004.01.005

Piatak NM, Parsons MB, Seal RR (2015) Characteristics and environmental aspects of slag: a review. Appl Geochem 57:236–266. doi:10.1016/j.apgeochem.2014.04.009

Potysz A, van Hullebusch ED, Kierczak J, Grybos M, Lens PNL, Guibaud G (2015) Copper metallurgical slags – current knowledge and fate, *Critical Reviews in*. Environ Sci Technol 45 (22):2424–2488. doi:10.1080/10643389.2015.1046769

Potysz A, Grybos M, Kierczak J, Guibaud G, Lens PNL, van Hullebusch ED (2016) Bacterially-mediated weathering of crystalline and amosphous Cu-slags. Appl Geochem 64:92–106. doi:10.1016/j.apgeochem.2015.07.011

Puziewicz J, Zainoun K, Bril H (2007) Primary phases in pyrometallurgical slags from a zinc-smelting waste dump, Swietochlowice, upper Silesia, Poland. Can Mineral 45:1189–1200. doi:10.2113/gscanmin.45.5.1189

Romero FM, Villalobos M, Aguirre R, Gutierrez ME (2008) Solid-phase control on lead bioaccessibility in smelter-impacted soils. Arch Environ Contam Toxicol 55:566–575. doi:10.1007/s00244-008-9152-3

Saha R, Saha N, Donofrio RS, Bestervelt LL (2013) Microbial siderophores: a mini review. J Basic Microbiol 53:303–317. doi:10.1002/jobm.201100552

Saikia N, Cornelis G, Mertens G, Elsen J, Van Balen K, Van Gerven T, Vandecasteele C (2008) Assessment of Pb-slag, MSWI bottom ash and boiler and fly ash for using as a fine aggregate in cement mortar. J Hazard Mater 154:766–777. doi:10.1016/j.jhazmat.2007.10.093

Saikia N, Cornelis G, Cizer Ö, Vandecasteele C, Gemert D, Balen K, Gerven T (2012) Use of Pb blast furnace slag as a partial substitute for fine aggregate in cement mortar. J Mater Cycles Waste Manage 14:102–112. doi:10.1007/s10163-012-0043-3

Seignez N, Bulteel D, Damidot D, Gauthier A, Potdevin JL (2006) Weathering of metallurgical slag heaps: multi-experimental approach of the chemical behaviours of lead and zinc. Waste Manage Environ iii 1:31–40. doi:10.2495/WM060041

Seignez N, Gauthier A, Bulteel D, Buatier M, Recourt P, Damidot D, Potdevin JL (2007) Effect of Pb-rich and Fe-rich entities during alteration of a partially vitrified metallurgical waste. J Hazard Mater 149:418–431. doi:10.1016/j.jhazmat.2007.04.007

Seignez N, Gauthier A, Bulteel D, Damidot D, Potdevin JL (2008) Leaching of lead metallurgical slags and pollutant mobility far from equilibrium conditions. Appl Geochem 23:3699–3711. doi:10.1016/j.apgeochem.2008.09.009

Sivry Y, Munoz M, Sappin-Didier V, Riotte J, Denaix L, De Parseval P, Destrigneville C, Dupré B (2010) Multimetallic contamination from Zn-ore smelter: solid speciation and potential mobility in riverine floodbank soils of the upper lot river (SW France). Eur J Mineral 22:679–691. doi:10.1127/0935-1221/2010/0022-2060

Uroz S, Calvaruso C, Turpault MP, Frey-Klett P (2009) Mineral weathering by bacteria: ecology, actors and mechanisms. Trends Microbiol 17:378–387. doi:10.1016/j.tim.2009.05.004

Van Alphen M (1999) Atmospheric heavy metal deposition plumes adjacent to a primary lead-zinc smelter. Sci Total Environ 236:119–134. doi:10.1016/S0048-9697(99)00272-7

van Hullebusch ED, Yin NH, Seignez N, Labanowski J, Gauthier A, Lens PNL, Avril C, Sivry Y (2015) Bio-alteration of metallurgical wastes by *Pseudomonas aeruginosa* in a semi flow-through reactor. J Environ Manag:297–305. doi:10.1016/j.jenvman.2014.09.018

Vdovic N, Billon G, Gabelle C, Potdevin JL (2006) Remobilisation of metals from slag and polluted sediments (case study: the canal of the Deule river, northern France). Environ Pollut 141:359–369. doi:10.1016/j.envpol.2005.08.034

Vítková M, Hyks J, Ettler V, Astrup T (2013) Stability and leaching of cobalt smelter fly ash. Appl Geochem 29:117–125. doi:10.1016/j.apgeochem.2012.11.003

Willscher S, Bosecker K (2003) Studies on the leaching behaviour of heterotrophic microorganisms isolated from an alkaline slag dump. Hydrometallurgy 71:257–264. doi:10.1016/S0304-386X(03)00164-6

Willscher S, Pohle C, Sitte J, Werner P (2007) Solubilisation of heavy metals from a fluvial amd generating tailings sediment by heterotrophic microorganisms. J Geochem Explor 92:177–185. doi:10.1016/j.gexplo.2006.08.013

Wu SC, Luo YM, Cheung KC, Wong MH (2006) Influence of bacteria on Pb and Zn speciation, mobility and bioavailability in soil: a laboratory study. Environ Pollut 144:765–773. doi:10.1016/j.envpol.2006.02.022

Yang Y, Li S, Bi X, Wu P, Liu T, Li F, Liu C (2010) Lead, Zn, and cd in slags, stream sediments, and soils in an abandoned Zn smelting region, southwest of China, and Pb and S isotopes as source tracers. J Soils Sediments 10:1527–1539. doi:10.1007/s11368-010-0253-z

Yin NH, Sivry Y, Avril C, Borensztajn S, Labanowski J, Malavergne V, Lens PNL, Rossano S, van Hullebusch ED (2014) Bioweathering of lead blast furnace metallurgical slags by *Pseudomonas aeruginosa*. Int Biodeterior Biodegrad 86:372–381. doi:10.1016/j.ibiod.2013.10.013

Yin NH, Sivry Y, Guyot F, Lens PNL, van Hullebusch ED (2016) Evaluation on chemical stability of lead blast furnace (LBF) and imperial smelting furnace (ISF) slags. J Environ Manag 180:310–323. doi:10.1016/j.jenvman.2016.05.052

Chapter 6
Leaching and Recovery of Metals

Manivannan Sethurajan, Piet N.L. Lens, Heinrich A. Horn, Luiz H.A. Figueiredo, and Eric D. van Hullebusch

Abstract Sludges, dusts, residues and other wastes originating from ferrous and non-ferrous metallic industries pose a serious environmental threat, if not disposed properly. Disposal of these wastes is expensive and remediation is a necessary step to be implemented to control the adverse environmental effects if disposal is done improperly. Since the past couple of decades, the world's high-grade metal reserves have been depleted considerably, but the demand for metals in day-to-day life in this electronic era is growing rapidly. The depletion of high-grade ores urges the mineral industry to look for alternative resources for metal extraction. Sludges, dusts, and other wastes generated by the metallurgical industries are interesting options as they still contain significant amounts of valuable base and heavy metals, sometimes even precious metals like gold and silver and also rare earth elements, depending on the nature of the mining site and composition of the primary ores used. This chapter overviews various hydrometallurgical and bio-hydrometallurgical leaching processes for the extraction of metals from these wastes. Different strategies of metal recovery such as solvent-extraction, electrowinning, bio/chemical sorption and bio/chemical precipitation from the

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M. Sethurajan • E.D. van Hullebusch (✉)
Université Paris-Est, Laboratoire Géomatériaux et Environnement (LGE), EA 4508, UPEM, 77454 Marne-la-Vallée, France

UNESCO-IHE Institute for Water Education, Delft, The Netherlands
e-mail: Eric.vanHullebusch@univ-paris-est.fr; e.vanhullebusch@un-ihe.org

P.N.L. Lens
UNESCO-IHE Institute for Water Education, Delft, The Netherlands

Department of Chemistry and Bioengineering, Tampere University of Technology, PO Box 10541, Tampere, Finland

H.A. Horn
Universidade Federal de Minas Gerais, NGqA-CPMTC, Instituto de Geociências, Av. Antônio Carlos, 6627, Pampulha, Belo Horizonte, MG 31270-901, Brazil

L.H.A. Figueiredo
Universidade Estadual de Montes Claros, Solos e nutrição de plantas, Avenida Reinaldo Viana, 2630, Bico da Pedra, Janauba, MG 39440-000, Brazil

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wastes generated by various ferrous and non-ferrous metallic industries are overviewed.

Keywords Metallurgical wastes • Secondary resources • Bio-hydrometallurgy • Metal recovery

Contents

6.1 Introduction

Owing to the enormous increase in the usage of metals in day-to-day life in the form of electronics, households, ornaments and accessories, the demand for metals is also increasing enormously (Anjum et al. 2012; Gahan et al. 2012). Metals are usually produced from mined mineral ores by ferrous and non-ferrous metallurgical industries. These metallurgical industries are not only producing metals, but also generating bulk quantities of wastes, which are either stored in reservoirs or disposed of in the environment. There are a lot of environmental issues associated with this practice (Lottermoser 2010). This review discusses in detail these different types of wastes, their composition and the environmental considerations. Due to the rapid industrialisation and the demand for metals, there is also a huge depletion of high-grade primary metal resources, which urges the metal producing industries to look for secondary alternative sources for metal extraction (Anjum et al. 2012). Metal bearing wastes from different industries can be such alternative resources for the recovery of metals, as some of the wastes still contain significant levels of valuable metals. In addition, also the adverse effects of the metals on the environment can also thus be reduced. The importance of waste utilisation and recycling has widely increased nowadays in view of the sustainable resource supply, circular economy, waste management and environmental protection. Secondary resources utilisation refers to the usage of waste as the feedstock for the manufacturing of products. This strategy helps the society in two ways: (i) the generation of waste is greatly reduced; consequently its disposal into the environment will also be reduced and (ii) it enables sustainable resource management as well as yielding economic benefits (Rao 2011).

In this chapter, up-to-date available methodologies for the extraction and recovery of base and heavy metals from different metallurgical wastes are discussed. Metal bearing wastes such as dusts and sludges from steel making industries and smelting processes and sludges and leach residues from metallurgical industries will be given a special focus, and their potential to be used as a secondary source for metal extraction will be highlighted. Their nature, elemental and mineralogical composition and various hydrometallurgical (chemical and biological) processes used for metal leaching and recovery will be overviewed.

6.1.1 Solid Wastes as Secondary Resources

There are a lot of studies on the effective utilisation of low grade ores to extract valuable metals in an economic as well as environment friendly manner (Anjum et al. 2012). Different approaches have been proposed for the extraction of heavy metals from industrial wastes (solid wastes and slurry wastes), such as metal rich wastewaters, fly ashes, spent liquors, spent catalysts, spent batteries, slags, shales and sludges, some of which have been patented (Brombacher et al. 1997). Jha et al. (2001) studied the proposed processes to recover zinc from various industrial wastes. Techniques for the utilisation of slags (Shen and Forssberg 2003) and sludges from the steel industries were reviewed by Das et al. (2006). Cui and Zhang (2008) overviewed the different pyrometallurgical and hydrometallurgical processes for the extraction of precious metals from electronic wastes. Lee and Pandey (2012) discussed the available methods for the extraction of various metals (Cu, Zn and Ni) from different industrial wastes by microbially assisted leaching processes. Erust et al. (2013) reviewed the possible applications of biohydrometallurgy to recover metals from spent batteries and spent catalysts. They overviewed biological approaches for the utilisation of secondary resources to supply some of the critical materials, e.g. platinum group elements and rare earths. Kaksonen et al. (2014) reported the ability of microbes to process and recover gold. Johnson (2014) discussed biomining and the possible biotechnological applications to extract metals from ores and waste materials.

6.1.2 Metallurgical Sludges, Dusts and Residues as Secondary Resources

Chemical and mineralogical characteristics and toxicity levels of metallurgical wastes are listed in Table 6.1. Table 6.1 clearly shows the high metal content (above sub-economic) of these waste materials. The toxicity characteristic leaching procedure (TCLP) values shown in Table 6.1 also suggest that at least one of the metal values fails to comply with environmental regulations, making them as 'hazardous' and preventing them from being disposed in the environment (Laforest and Duchesne 2006; Erdem and Özverdi 2011; Li et al. 2013; Tutor et al. 2013). In a few instances, Portland cement, ferrous sulphate or glass cullets are mixed with these metallurgical wastes to solidify them and make them more stable (Pereira et al. 2001; Salihoglu and Pinarli 2008; Bulut et al. 2009). In any case, the valuable metals harboured by these solid wastes are wasted. The toxicity levels of these metallurgical wastes form the basic necessity of finding a solution to treat or to reuse them in order to reduce their environmental impacts. Moreover, the mineralogical characteristics indicate the potential of these metallurgical solid wastes to be a secondary resource for metal recovery.

6.2 Wastes from the Metal Producing Industry

Natural ores consist of the desired metal present in high concentrations in combination with inherent waste compounds, i.e. metals or elements not important for the production process and usually present in lower concentrations. For example, nearly 50% of a zinc concentrate consists of unwanted elements like sulphur, iron, lead, titanium, silicon, copper, calcium, manganese, cadmium, magnesium, arsenic and mercury (Reuter et al. 1998). The metal of interest can be found in its oxidic or sulphidic form, as primary or secondary metallic phases or any other form in the natural ore. Many metallurgical processes, starting from open pit mining to final purification, have to be done to separate the pure metal from the ore. Usually some kind of waste is generated at each step of the metallurgical process; thus the metallurgical industries not only produce metals, but also deposit a huge load of waste materials in the environment (Leonard 1978; Chandrappa and Das 2012). The wastes generated by the metallurgical industries are huge and they are mostly disposed of in the environment (Fig. 6.1). Certain wastes not only contain unwanted elements, but have also considerable quantities of metals, mostly as oxides or sulphides.

Table 6.1 Chemical, mineralogical and toxicological characteristics of metallurgical wastes

Source	Major mineral phases	Chemical composition and metal content (%)	Potential toxicity	Binders	References
Electric arc furnace dust (steel industry)	Fe_3O_4	Cr – 10.9	(TCLP, US EPA 1311, pH 2.88)	–	Laforest and Duchesne (2006)
	Fe_2O_3	Ni – 4.1	Cr_{total} – 9.7 mg L^{-1}		
	MgO	Pb – 1.4	Cr (VI) – 6.1 mg L^{-1}		
	$FeCr_2O_4$	Zn – 5.2	Ni – 2.3 mg L^{-1}		
	$ZnFe_2O_4$		Pb – 0.4 mg L^{-1}		
			Zn – 93.9 mg L^{-1}		
Electric arc furnace dust (steel industry)	–	As – 0.29	(TCLP, DIN 38414-S4, pH 7)	–	Pereira et al. (2001)
		Cd – 0.08	Cd – 0.5 mg L^{-1}		
		Cr – 0.95	Cr – 5 mg L^{-1}		
		Ni – 0.20	Pb – 5 mg L^{-1}		
		Pb – 1.30	Zn – 300 mg L^{-1}		
		Zn – 26.0			

(continued)

Table 6.1 (continued)

Source	Major mineral phases	Chemical composition and metal content (%)	Potential toxicity	Binders	References
Ferrochrome arc furnace dust (steel industry)	–	Mg – 17.18	(TCLP, US EPA 1311, pH 2.88)	PC – sand – $FeSO_4$ mixture (5 stoichiometric: 30%: 16%) is used with the dust to make environmentally stable	Bulut et al. (2009)
		Cr – 13.90	Cr – 9.81 mg L^{-1}		
		Si – 10.13	Zn – 103.85 mg L^{-1}		
		Fe – 5.19			
		Al – 2.83			
		Zn – 1.50			
		Ca – 0.99			
		Cu – 0.03			
		Mn – 0.18			
		Ni – 0.13			
		Pb – 0.02			
		Ti – 0.07			
Arsenopyrite mining sludge (abandoned mining site)	$FeAsO_4·2H_2O$	As – 0.015	As – 11.2 mg L^{-1}	–	Tutor et al. (2013)
	$KFe_4(AsO_4)_3(OH)_4·(6–7)H_2O$				
	α-FeOOH)				

Zinc extraction residue (zinc industry)	$PbSO_4$	Pb – 19.02	(TCLP, US EPA 1311, pH 2.88)	–	Özverdİ and Erdem (2010)
	Fe_2O_3	Zn – 7.98	Zn – 362 mg L^{-1}		
	$CaSO_4.0.5H_2O$	Fe – 5.44	Pb – 65.10 mg L^{-1}		
		Cd – 0.024	Cd – 2.88 mg L^{-1}		
			Mn – 3.47 mg L^{-1}		
Zinc extraction residue (zinc industry)	$PbSO_4$,	Pb – 19.02	–	Minimum 40% of Portland cement (PC) should be blended to the residue to make stable and solidified	Erdemand Özverdİ (2011)
	$CaSO_4 \cdot 2H_2O$,	Zn – 7.98			
	$ZnSO_4 \cdot 2H_2O$	Fe – 5.44			
		Cu – 0.065			
		Cd – 0.024			
Zinc leach residue (zinc industry)	$ZnFe_2O_4$	Fe – 24.02	(TCLP, US EPA 1311, pH 2.88)	–	Li et al. (2013)
	$ZnSO_4$	Zn – 19.57			

(continued)

Table 6.1 (continued)

Source	Major mineral phases	Chemical composition and metal content (%)	Potential toxicity	Binders	References
			Zn – 4589 mg L^{-1}		
	$CaSO_4$	Ca – 1.97	Pb – 1.4 mg L^{-1}		
	PbS	Pb – 4.18	Cd – 93.5 mg L^{-1}		
	$PbSO_4$	Mn – 1.41	As – 0.3 mg L^{-1}		
	Pb_3SiO_5	Cu – 0.91			
	Zn_2SiO_4	Mg – 0.37			
Zinc leach residue (zinc industry)	–	Fe – 13.6	(TCLP, US EPA 1311, pH 2.88)	Neutralisation sludge (NS) mixed to the zinc leach residue in the mass ratio of 8:2 to make the residue stable	Ke et al. (2014)
		Zn – 5.0	Zn – 3499.5 mg L^{-1}		
		Ca – 3.3	Pb – 5.17 mg L^{-1}		
		Pb – 5.40	Cd – 67.75 mg L^{-1}		
		Cd – 0.15	Cu – 82.35 mg L^{-1}		
		Cu – 0.26			

Zinc leach residue (ZLR1) (zinc industry)	$CaSO_4.2H_2O$	Ca – 8.64	(TCLP, US EPA 1311, pH 2.88)	–	Sethurajan et al. (2016a)
	SiO_2	Fe – 6.67	Pb – 8.83		
	Fe_3O_4	Zn – 5.01	Cu – 27.87		
		Pb – 1.78	Cd – 27.05		
		Mn – 0.99	Zn – 1052.72		
		Cu – 0.2			
		Cd – 0.06			
Zinc leach residue (ZLR2) (zinc industry)	$CaSO_4.2H_2O$	Ca – 7.89	(TCLP, US EPA 1311, pH 2.88)	–	Sethurajan et al. (2016a)
		Fe – 9.58	Pb – 10.39		
		Zn – 2.73	Cu – 2.06		
		Pb – 1.53	Cd – 9.05		
		Mn – 0.29	Zn – 349.29		
		Cu – 0.07			
		Cd – 0.04			
Zinc leach residue (ZLR3) (zinc industry)	$CaSO_4.2H_2O$	Ca – 6.95	(TCLP, US EPA 1311, pH 2.88)	–	Sethurajan et al. (2016a)
		Fe – 11.5	Pb – 3.94		
		Zn – 2.51	Cu – 13.16		
		Pb – 2.35	Cd – 3.19		
		Mn – 0.05	Zn – 94.65		
		Cu – 0.14			
		Cd – 0.02			

‘–’ = not available

US EPA United States Environmental Protection Agency, *TCLP* Toxicity Characteristics Leaching Procedure, *DIN* German Standardization Organization

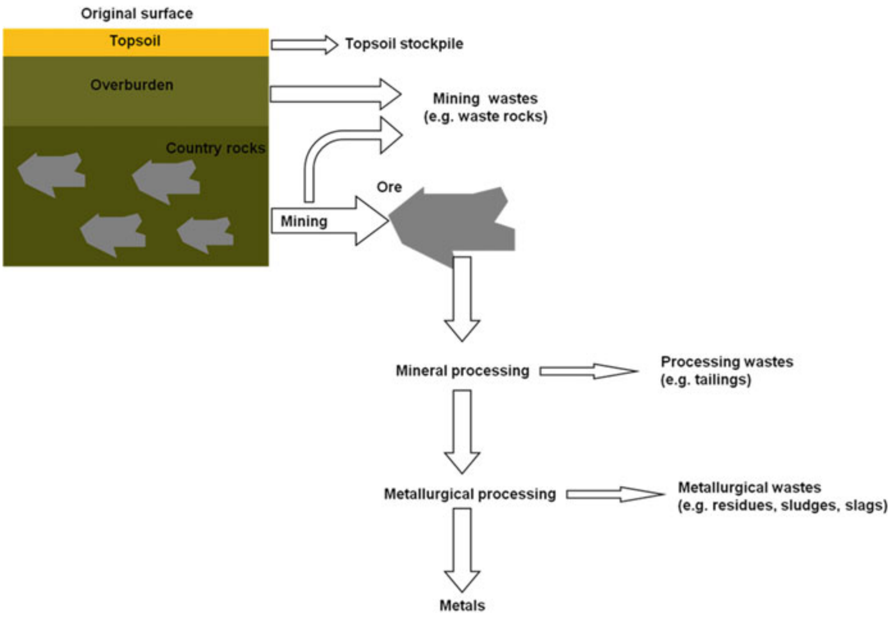


Fig. 6.1 Schematic product and waste streams from mining to metal refining (Adapted from Lottermoser 2010). Note the generation of wastes at each and every step of mining and metallurgical processes

Metallurgical industries produce solid, liquid and gaseous wastes. These can be classified as (i) mining wastes, (ii) processing wastes and (iii) metallurgical wastes (Lottermoser 2010). Mining wastes are produced during the initial stages of mining operations like ‘open pit’ or ‘underground’ mining. These operations usually produce waste rocks, overburden, spoil and atmospheric emissions. These mining wastes contain very low levels of or even no metals. Processing wastes are wastes generated by physical ore processing processes applied prior to the extraction of metals, like washing, magnetic separation, gravity separation, crushing, milling, size reduction and floatation (Leonard 1978; Lottermoser 2010). Wastewater streams resulting from the washing and also the mine tailings are categorised as processing wastes. Some of the mine tailings contain significant concentrations of metals and are prone to bioweathering and leaching. Most of them are used for backfilling working sites or reclamation and reconstruction of mining areas, as they do not contain economic levels of metals (Wong 1986).

Metallurgical wastes are mostly residues or muds which are produced at the final stage of the extractive metallurgy and cannot be treated commercially. Extractive metallurgy can be hydrometallurgy, pyrometallurgy or electrometallurgy. Hydrometallurgy involves solvents for the metal extraction, whereas pyrometallurgy involves heat and electrometallurgy involves electric current. These processes

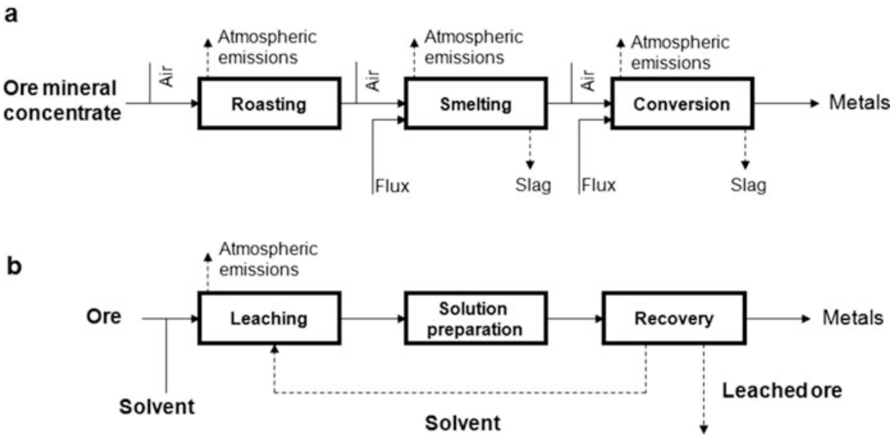


Fig. 6.2 Simplified flow charts of (**a**) pyrometallurgical and (**b**) hydrometallurgical operations, in which ore is treated to yield metals accompanied by the generation of wastes (Redrawn from Lottermoser 2010)

separate the metals from their processed ores and also generate vast amounts of metallurgical wastes, like gaseous emissions, dust, slags, sludges, muds, spent ore and residues (Fig. 6.2).

Metallurgical wastes contain considerable concentrations of metals, depending on the mineralogy of the ore and geography of the ore mining site. Disposal or storage of these wastes needs to be done carefully because of the adverse environmental impacts such as release of heavy metals by weathering (Gieré et al. 2003; Kierczak et al. 2009), contamination of water bodies (Johnson 2009), metal incorporation into the food chain (Kachur et al. 2003), formation of efflorescences i.e. metal hydrosulphates as a result of evaporation (Keith et al. 2001; Sánchez-España et al. 2005; Romero et al. 2006) or creation of acidic environments (Hammarstrom et al. 2005).

6.2.1 Dusts

Flue dusts are fine, metal containing dust particles collected at the gas exhaust of smelters or any other furnace during metallurgical processing. Copper and zinc producing industries are the major sources of waste dust generation. According to Davenport et al. (2002), dusts emanating from copper smelters consist of 20–40 mass percent of Cu and can be either recycled with concentrates or can be treated by hydrometallurgy for further metal recovery. Massinaie et al. (2006) reported that these wastes originating from copper industries are mostly rich in chalcocite (Cu_2S), chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4) and covellite (CuS).

Similarly, metallic dusts are generated during the steel making processes in e.g. electric arc furnace (EAF) smelters. These EAF dusts are rich in zinc and iron oxides and are generated during the heating and cooling of the smelting processes and collected at the gas cleaning system of scraps (Jha et al. 2001). Electric arc furnaces dusts from steel industries typically contain 19.4% Zn, 24.6% Fe, 4.5% Pb, 0.42% Cu, 0.1% Cd, 2.2% Mn, 1.2% Mg, 0.4% Ca, 0.3% Cr, 1.4% Si and 6.8% Cl (Caravaca et al. 1994).

Blast furnace (BF) dusts are similar to EAF, generated during the wet cleaning of the gases in blast furnace mediated steel production. Upon emission, dusts agglomerate after long-term exposure to the earth's atmosphere because of its inherent moisture content. Elemental analysis revealed that these BF dusts mostly contain iron and carbon in high concentrations. The typical composition of BF dusts is carbon (~30%), Fe_2O_3 (~51%), SiO_2 (~7%), Al_2O_3 (~3%) and other metals such as Zn, Pb and Mn (Zeydabadi et al. 1997; Das et al. 2002).

6.2.2 *Sludges*

Sludges are co-products generated during various stages in ferrous and non-ferrous industries. They can be blast furnace sludges (BFS), electric arc furnace sludges (EAFS), converter sludges, basic oxygen furnaces sludges (BOFS) from steel-making industries, sludges from plating industries and also sludges from metal-producing industries. Steel-making industries generate significant quantities of sludge (2–4 tonnes of wastes per tonne of steel (Das et al. 2006)), which consists of approximately 2.5% of Zn and 61% of Fe (Trung et al. 2011). Mansfeldt and Dohrmann (2004) studied the mineralogical and chemical composition of the pig-iron-making sludges and found that, apart from the iron mineral phases magnetite (Fe_3O_4, 3%), hematite (Fe_2O_3, 4%) and wuestite (FeO, 2%), they also contain primary and secondary phases of the metals Zn (3%), Pb (1%), Cd (0.01%), and As (0.1). The sludges from the metallurgical industries are also polymetallic, containing significant mass concentrations of Fe 44%, S 28%, As 0.38%, and Zn 0.13% (Hita et al. 2006, 2008). The mineralogical and elemental composition of the metallurgical sludge depends on the nature of the ores.

6.2.3 *Residues*

Residues can be mainly classified as leach residues and purification residues, based on their generation during the operational processes. Purification residues are produced during the separation of the pure zinc metal from its impurities (for e.g. copper and cobalt), while leach residues are derived during the filtration of the purified acid (mostly sulphuric acid) leached products prior to electrolysis. Recovery of metals from plant residues, like zinc plant residues (ZPR), has gained importance in recent years. Copper and cobalt are often found in the residues generated at the end of zinc-production processes.

There are only few investigations on the extraction of these metals from ZPR. Min et al. (2013) investigated the chemical and mineralogical composition of the leaching residues generated during zinc and lead hydrometallurgical operations. They found that ZPR consist of (mass fractions) 5.35% Zn, 4.66% Pb, 0.24% Cu, 0.15% Cd, 0.25% As and 13.54% Fe. Usually the presence of zinc ferrites, which is a spinel ($ZnFe_2O_4$) resulting from the desulphurisation of iron containing sphalerite ores in the final leach residues, makes the extraction of metals tedious because of its very stable and insoluble nature.

6.3 Leaching

Leaching is the key unit operation in metallurgical processes. It is the dissolution of metals from their natural ores into a liquid medium. Leaching processes are classified based on the method used for the leaching of metals, i.e. hydrometallurgy (chemicals) or bio-hydrometallurgy (microbial mediated leaching). Different leaching processes and the leaching of metals from various metal bearing solid wastes are discussed in detail below.

6.3.1 Hydrometallurgical Processes

Hydrometallurgy is the extraction of metals from resources with the help of aqueous chemicals. Hydrometallurgical processes have a few advantages over pyrometallurgy, as they are more eco-friendly and economic for low-grade metal reserves. A general process flow diagram of hydrometallurgy is illustrated in Fig. 6.3. Hydrometallurgy is a general term which refers to a range of processes, including chemical leaching or mediated by oxidising agents, higher oxygen partial pressure or microbial activity (National Research Council 2002).

Hydrometallurgical processes consist of different steps: (i) leaching of metals from the source and dissolution into the leachate, (ii) separation of the metal-loaded leachate from the residues, (iii) recovery of the metals from the leach solution and (iv) regeneration and reuse of the leachate (Ghosh and Ray 1991). Leaching processes can be done *in situ* (heaps or dumps) or *ex situ* (reactors or vessels). There are various parameters which affect the leaching behaviour of metals from their parent material: (i) pH, (ii) temperature, (iii) concentration of the leaching agent(s), (iv) solid-to-liquid phase ratio and (v) particle size of the parent material.

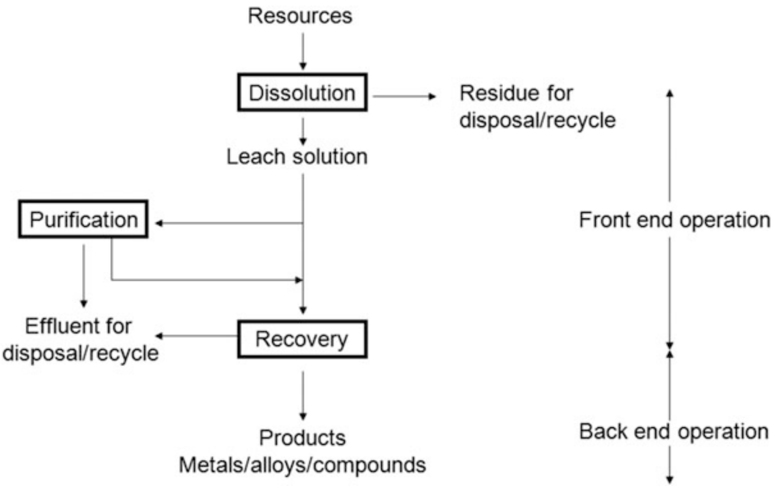


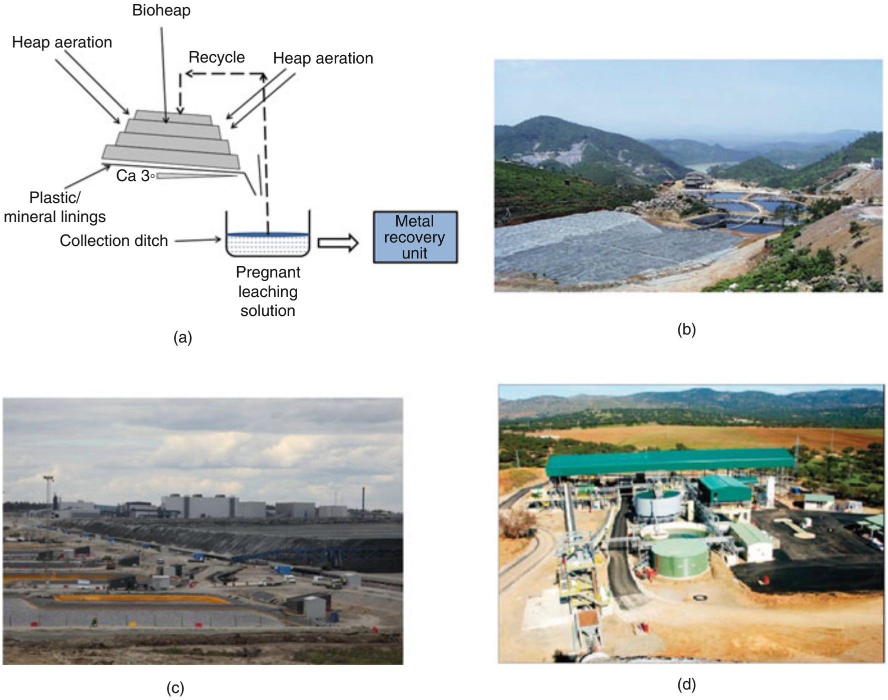
Fig. 6.3 Basic unit processes in hydrometallurgy (Redrawn from Gupta 2006)

The efficiency of hydrometallurgical processes is increased by using improved leaching conditions coupled to high-pressure leaching and ultra-fine grinding (Malhotra et al. 2009). Selective leaching of metals can also be achieved by adjusting the pH or working at elevated temperatures and pressures (Trefry and Metz 1984; National Research Council 2002; Havlik et al. 2004).

6.3.2 Biohydrometallurgical Processes

Biohydrometallurgy is a recent advancement in the mining industry where micro-organisms are used to enhance the leaching of metals and biotechnological processes are used for the recovery of the dissolved metals. Biohydrometallurgy is the conversion of insoluble metals in ores (or other sources like metallurgical wastes) to the soluble form with the help of micro-organisms. Microbial extraction and recovery of metals like Cu has received considerable attention in the past three decades owing to its relative simplicity, eco-friendly operation and low capital requirement when compared to those of the conventional chemical/heat treatment processes (Olson et al. 2003; Watling 2006; Johnson 2013). Commercial applications of bioleaching were also reported in many instances (Brierley and Brierley 1999, 2001; Brierley 2008; Neale et al. 2011; Gahan et al. 2012). A simplified bioheap leaching process and commercial bioleaching plants are given in Fig. 6.4.

Knowledge and understanding the metal – microbe interactions and the mechanisms of bioleaching are much needed for the effective recovery of metals from metallurgical wastes.



(a) (b)

(c) (d)

Fig. 6.4 Bioleaching process and commercial bioheap leaching plants: (**a**) schematic representation of the bioheap leaching process, (**b**) bioleaching plant in Zijinshan copper mine, China (Renman et al. 2006), (**c**) bioheap leaching plant in Talvivara mining company, Finland (Riekkola-Vanhanen 2010) and (**d**) bioheap leaching plant in Kasese mine, Uganda (Gahan et al. 2012)

6.3.2.1 Microbe – Metal Interactions

Bacteria and fungi are able to extract metals from metal contaminated soils and metal wastes. These micro-organisms use one of the following processes (Fig. 6.5): (i) non-specific interaction of metal ions with cationic binding sites present outside the cell wall, (ii) specific interactions at the periplasmic sites of the cell wall, (iii) metallo-chemical complex (chemicals secreted by the microbes in the surrounding medium and the metals form a complex) uptake by the cells, (iv) bioaccumulation, (v) metal precipitation by the microbial metabolites or (vi) metal volatilisation (Upadhyay 2002).

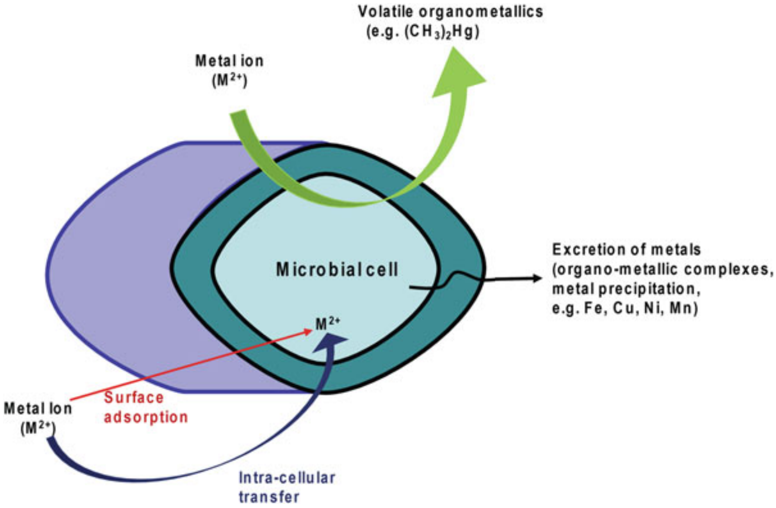


Fig. 6.5 Microbe-metal interactions that can be engineered to develop enhanced bioleaching processes (Reproduced from Upadhyay 2002)

6.3.2.2 Bioleaching

Microbes leach metals via various processes (Fig. 6.6): (i) acidolysis, (ii) redoxolysis, (iii) complexolysis and (iv) bioaccumulation (Schinner and Burgstaller 1989; Bosshard et al. 1996; Brandl 2001; Wu and Ting 2006). Recently, reductive dissolution of oxidised Ni-laterites ores was also reported (Johnson et al. 2013).

The most commonly used genera to catalyse the bio-oxidation of sulphides and liberate the desired metals into the liquid phase are chemo-litho-autotrophic bacteria oxidising iron, e.g. *Leptospirillum* spp. (Sand et al. 1992; Falco et al. 2003; Sethurajan et al. 2012), *Ferroplasma* spp. (Edwards et al. 2000; Golyshina et al. 2000) and *Ferrimicrobium* spp. or sulphur, e.g. *Acidithiobacillus* spp. (Kelly and Wood 2000; Falco et al. 2003), *Thiomonas* spp. (Han et al. 2013) and *Sulfolobus* spp. (Norris et al. 2000). These microbes obtain energy by oxidising ferrous into ferric ion and elemental sulphur to sulphuric acid (Rawlings 2005), thereby leaching reduced sulphide minerals. The bacteria thus enable oxidative dissolution and acidolysis by producing the ferric ions and sulphuric acid.

The mechanisms by which *Acidithiobacillus ferrooxidans (A. ferrooxidans)* leaches out the metal constituents are (Crundwell 2003): (i) direct bioleaching (bacteria adhere on the surface of the ores and oxidise the reduced sulphides) and (ii) indirect bioleaching (bacteria oxidise the ferrous to ferric ion, thereby contributing to the leaching of minerals). This indirect bioleaching by ferric ion can be subdivided into two phenomena: the produced ferric ions are released either into the bulk solution or inside the layer between bacteria and exopolymeric material affecting the mineral surface and thus leach out minerals.

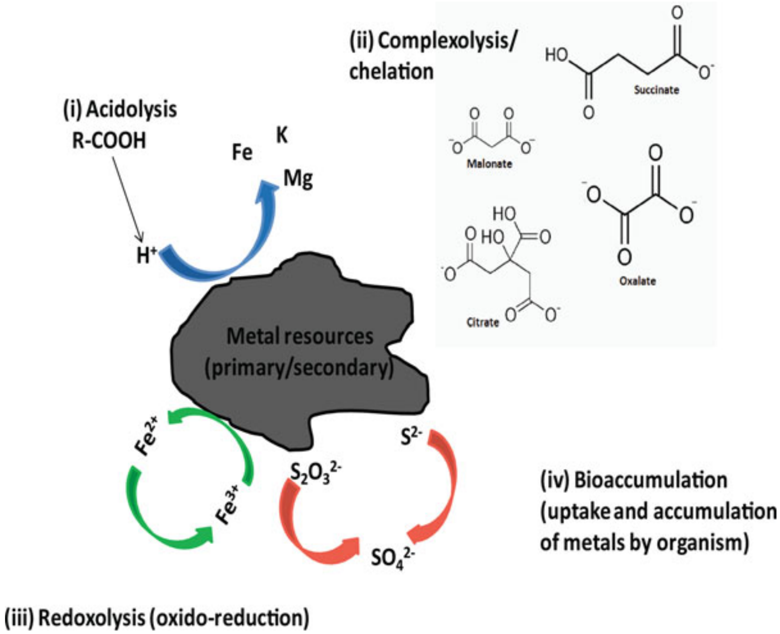


Fig. 6.6 Mechanisms of bioleaching of metals from primary and secondary resources (Adapted from Uroz et al. 2009)

The generalised reactions (R1 and R2) for the bio-oxidation of mineral sulphides leading to (precious) metal leaching are:

$$\text{Direct leaching}: \quad MS + 2O_2 \rightarrow MSO_4 \tag{R1}$$

$$\text{Indirect leaching}: \quad MS + Fe_2(SO_4)_3 \rightarrow MSO_4 + 2FeSO_4 + S^o \tag{R2}$$

where M is a bivalent metal.

Various heterotrophic bacteria, e.g. *Pseudomonas* spp. (Müller et al. 1995; Lingling et al. 2012; Pradhan and Kumar 2012) and *Bacillus* spp. (Farbiszewska-Kiczma et al. 2004) as well as fungi, e.g. *Aspergillus* spp. (Mulligan et al. 1999, 2004; Rao et al. 2002), *Penicillium* spp. (Acharya et al. 2002; Amiri et al. 2011; Ilyas et al. 2013) and *Ganoderma* spp. (Nouren et al. 2011) have also been investigated for their ability to bioleach metals. In few instances, gold bioleaching by cyanide producing bacteria were also reported (Chi et al. 2011; Işıldar et al. 2016). Mixed cultures of two or more bacteria or indigenous enrichments of microbes from metal contaminated sites were studied for metal solubilisation from the ores and achieve higher efficiencies than pure cultures (Sandstrom and Petersson 1997; Fu et al. 2008; Plumb et al. 2008).

Fungal bioleaching mechanisms mainly follow acidolysis, i.e. solubilisation of the metals by the acidic dissolution (protonation of oxygen atom) from the parent material (Burgstaller and Schinner 1993). These fungi produce organic acids like citric, oxalic, malic or gluconic acid (Mulligan et al. 2004; Johnson 2006). *Aspergillus* spp. are the most-studied fungi for the bioleaching processes because of their capacity to produce higher levels of organic acids. Acharya et al. (2002) and Sukla and Panchanadikar (1993) studied *Penicillium* sp. for the bioleaching of valuable metals from low-grade ores. Sukla et al. (1995) investigated the bioleaching of Sukinda lateritic Ni ore using the fungus *Penicillium* spp. and reported that, under optimum conditions of pulp density, dextrose concentration and ore size fraction, a maximum of 90% Co, 40% Mn and 12% Ni could be leached.

6.3.3 (Bio)Hydrometallurgical Treatment of Wastes from Metal Industries

6.3.3.1 Dusts

Dusts from the metallurgical industries contain significant amounts of metals. Various researchers used chemical and microbial mediated leaching procedures for the release of heavy metals from these wastes. Different (bio)hydrometallurgical approaches to processing these dusts from the metal industry for the leaching of metals were developed (Table 6.2). Cole et al. (1987) and Gabler and Jones (1988) studied the possibilities of re-using Zn from Brass smelter flue dust and secondary copper converter dust by sulphuric acid and ammonium carbonate, respectively. The recovered Zn was suitable for electrogalvanising and the ZnO could be re-fed to the furnace. Vítková et al. (2011) investigated the effect of pH on the leachability of metals from Cu smelter dusts and found that an acidic pH (pH 3) favoured the maximum leaching of the metals. As these dusts from the copper industries mainly consist of reduced mineral phases of metals, bioleaching is considered as an eco-friendly approach (Rossi 1990; Schnell Henry 1997; Oliazadeh et al. 2006). *Acidithiobacillus* spp. and *Leptospirillum* spp. are the genera widely used for the biological leaching of metals from metallurgical dusts. More than 70% of Zn was extracted by *A. ferrooxidans* from industrial Fe-Mn alloy dust (Solisio et al. 2002). Mixed populations of iron-oxidising and sulphur-oxidising bacteria were proposed to be more efficient than solely the pure cultures. Bakhtiari et al. (2008a, b, 2010) investigated the leaching efficiency of mixed cultures of *A. ferrooxidans*, *Acidithiobacillus thiooxidans (A. thiooxidans)* and *Leptospirillum ferrooxidans* (*L. ferrooxidans)* in different bioreactor configurations like continuous stirred tank reactors (CSTR) and air-lift bioreactors from different metal-bearing dust

Table 6.2 Different (bio)hydrometallurgical approaches proposed for the leaching of heavy metals from metallurgical dusts

Dust type (metal content – %)	Treatment	Leaching yield	References
Brass smelter flue dust	H_2SO_4 leaching	More than 90% of Zn was dissolved by using 0.18 kg L^{-1} of H_2SO_4 (pH 4–5, temperature 90 °C) in 1 h. Leached Zn used for electrogalvanising	Cole et al. (1987)
Zn – 66%			
Cu – 0.88%			
Fe – 0.24%			
Secondary copper converter dust	$(NH_4)_2CO_3$ and NH_4OH leaching	66% of Zn was dissolved by using 117 mg L^{-1} of NH_3, 94 g L^{-1} of CO_2 at room temperature, in 15 min leaching. Reusable ZnO and metal values from secondary copper smelter flue dusts were achieved	Gabler and Jones (1988)
Zn – 40.4%			
Cu – 0.86%			
Fe – 0.16%			
Pb – 16%			
Cu smelter dust	CEN/TS 14997:2006 protocol	80% of the total Cd, 30–40% Cu, Zn and Co, 17% Ni and only 2% Pb were released at pH 3 (HNO_3) in 48 h	Vítková et al. (2011)
Zn – 0.22 %			
Cu – 27.2%			
Fe – 19.3%			
Pb – 0.21%			
Fe-Mn alloy industrial dust	Bioleaching by *A. ferrooxidans*	Maximum of 76% of Zn recovered, when the conditions were: 1% pulp density, pH 2, 250 rpm, and temperature 30 °C	Solisio et al. (2002)
Zn – 5.5%			
Cu – 0.052%			
Pb – 0.29%			
Copper smelter flue dust	Mixed mesophilic (*A. ferrooxidans, A. thiooxidans* and *L. ferrooxidans*) bioleaching in CSTR	Maximum 85.5% of Cu after 23 days at 2.7% pulp density	Bakhtiari et al. (2010)
Zn – 1.67%			
Cu – 22.2%			
Fe – 5.9%			
Pb – 1.54%			
Flue dust of the Sarcheshmeh copper smelter	Mixed culture of *A. ferrooxidans, A. thiooxidans* and *L. ferrooxidans* airlift bioreactors	Maximum 90% of Cu at 2.7% pulp density after 2 days	Bakhtiari et al. (2008a)
Cu – 35.8%			
Fe – 15.3%			
Copper flue dust	*A. ferrooxidans, A. thiooxidans* and *Leptospirillum* mixed cultures in CSTR's	Maximum 89% of Cu at 2% pulp density after 2.7 days	Bakhtiari et al. (2008b)
Cu – 35.8%			
Fe – 15.3%			

(continued)

Table 6.2 (continued)

Dust type (metal content – %)	Treatment	Leaching yield	References
Copper mining flue dust	Mixed culture of *A. ferrooxidans* and *A. thiooxidans* in an agitated bioreactor	Cu recovery was 87% after 22 days in shake flask and 91% in bioreactor after 6.5 days	Massinaie et al. (2006)
Cu – 29.15%			
Fe – 22.23%			
Copper mining flue dust	Mixed culture *of* *A. ferrooxidans* and *A. thiooxidans*	Maximum 87% of Cu after 22 days at 5% pulp density	Oliazadeh et al. (2006)
Cu – 29.15%			
Fe – 22.23%			

samples. They reported that a maximum of 90% of Cu was leached within 2 days at lower solid to liquid phase ratios (2.7%) in air-lift bioreactors configurations.

The bioleaching efficiency of copper from smelter dusts (combined with flotation concentrate) was higher in the stirred tank reactors than in airlift bioreactors (Vakylabad et al. 2012) and thermophilic lithotrophs were slightly better bioleaching bacteria than mesophilic lithotrophs, although the impact of temperature was not very high as observed in the case of primary (chalcopyrite) ores (Vakylabad 2011; Vakylabad et al. 2012).

As with Cu dusts, there are numerous hydrometallurgical processes developed for the utilisation of EAF dusts. Conventionally, these dusts are treated by sulphuric acid (Duyvesteyn et al. 1979; Pearson 1981; Duyvesteyn and Jha 1986; Cruells et al. 1992). The efficiency of acidic leaching is greatly affected by the iron/zinc ratio and the presence of halogens, as these will interfere during the electrolysis (Havlik et al. 2004, 2006). Alkaline leaching is an alternative strategy for overcoming these problems. Xia and Picklesi (2000) proposed microwave assisted caustic leaching for the recovery of zinc from EAF dust and were able to extract more than 90% of Zn at 8 M NaOH at 117 °C. Dutra et al. (2006) demonstrated that 6 M NaOH at 90 °C recovered 74% of Zn from EAF dusts within 4 hours.

6.3.3.2 Sludges

Different hydrometallurgical approaches to processing metallurgical sludges for the effective and economic extraction of metals have been developed (Table 6.3). The use of hydrometallurgical operations for the effective extraction of Zn and Pb from BFS was reported by Van Herck and Vandecasteele (2000), who focused on the effect of the pH and redox potential. Silva et al. (2005) investigated various factors (pulp density, stirring, concentration of leachant and particle size) affecting the leaching of metals from galvanic sludges and stated that 1 M of H_2SO_4 can leach 88.6% Cu, 98.0% Ni and 99.2% Zn at room temperature in 24 h. Trung et al. (2011)

Table 6.3 Different (bio)hydrometallurgical approaches proposed for the leaching of heavy metals from metallurgical sludges

Sludge type (metal content – %)	Treatment	Leaching yield	References
Basic oxygen furnace sludge	H_2SO_4 leaching	81% of Zn recovered from the sludge (particle size >38 μm) by sulphuric acid (pH 2) and 18% of Fe recovered with H_2SO_4 (at pH 2) within 15 min	Kelebek et al. (2004)
Zn – 1.35%			
Fe – 55.9%			
Pb – 0.65%			
Basic oxygen furnace sludge	H_2SO_4 leaching	70% of Zn leached by 1 M H_2SO_4 at 80 °C within 15 min	Trung et al. (2011)
Zn – 2.74%			
Cu – 0.1%			
Fe – 47.7%			
Basic oxygen furnace sludge	5 M NaOH	Approximately 95% of the zinc was selectively removed after three leaching steps of the treated sludge with NaOH, at 400 °C	Cantarino et al. (2012)
Zn – 4.37%			
Fe – 50.65%			
Pb – 0.068%			
Cr – 0.023%			
Cd <0.02%			
Converter sludge from steel production	Bioleaching with mixed culture of *Acidithiobacillus* spp. and *Leptospirillum* spp.	100% Zn leached after 79 days at pH 0.5	Vestola et al. (2010)
Zn – 1.7%			
Cu – 0.02%			
Fe – 60.2%			
Pb – 0.09%			
Sludge from Ni/Cr plating plant	Sulphuric acid and ammoniacal leaching	88.6% Cu and 99.2% Zn by acid leaching	Silva et al. (2005)
Zn – 2.96%			
Cu – 4.2%			
Fe – 1.53%			
Pb – 0.36%			
Pyritic sludge – (Aznalcóllar, Spain)	Bioleaching with iron oxidising bacteria (*A. ferrooxidans, A. caldus*), and archaea (*S. metallicus*)	Approximately 90% of total Zn was recovered in 10 days, pH 2, temperature 65 °C by *S. metallicus*	Hita et al. (2008)
Zn – 0.13%			
Fe – 44%			

reported that at high temperature (80 °C), approximately 70% of Zn can be leached within 15 minutes by using 1 M H_2SO_4. Vereš et al. (2012) investigated the extraction of Zn from blast furnace sludge by microwave-assisted procedures. Cantarino et al. (2012) reported the selective leaching of zinc from basic oxygen furnace sludge with a three step leaching procedure (5 M NaOH) coupled to a thermal treatment, and extracted 95% of Zn.

Bioleaching of a steel-plant sludge using *A. ferrooxidans* was studied by Bayat et al. (2009). *A. ferrooxidans* extracted comparatively less metals (35% of Zn and 37% of Fe), which might be due to the oxidised mineral phases present in the metallurgical sludge (Fe_3O_4 and Fe_2O_3). Metallurgical sludges containing sulphidic minerals can be treated by microbial processing by oxidative dissolution, as acidic leaching involves concentrated acids and high temperatures and is thus expensive. Hita et al. (2008) reported the possibility of bacterial leaching (*A. ferrooxidans, Acidithiobacillus caldus* and *Sulfolobus metallicus*) of Fe, Zn and As from pyritic metallurgical sludge.

6.3.3.3 Residues

Hydrometallurgical extraction of zinc, especially from sulphidic ores, results in the generation of leach and purification residues. Different pyrometallurgical and hydrometallurgical leaching processes have been developed for the extraction of metals from these metallurgical residues (Table 6.4). Ngenda et al. (2009) proposed a new thermal treatment coupled to a highly concentrated acid leaching for the extraction of Zn from the zinc plant residues (ZPR) obtained from the Kolwezi Zinc Plant (Republic of Congo). Safarzadeh et al. (2009) extracted almost 99% of Zn from the zinc residues by 1.7 M sulphuric acid. Lu et al. (2014) demonstrated that 99% of Zn, Cd and Co can be extracted from purification residues by 48 g L^{-1} sulphuric acid. Sethurajan et al. (2017a) reported that hot (80 °C) sulphuric acid (1.5 M) can leach more than 70–90% of the Zn from Zn-hydrometallurgical residues.

The metal release kinetics follow the shrinking core model for the extraction of metals from ZPR (Safarzadeh et al. 2009, 2011; Sethurajan et al. 2017a). Safarzadeh et al. (2009) proposed that the addition of sulphuric acid, particle size, temperature and phenol dosage play an important role in the reductive leaching of manganese and cobalt. In some cases, e.g. residue from a Zn metallurgical plant in the Çinko-Kurşun metal industry (Turkey), the residues obtained during the hydrometallurgical extraction of Zn with a concentrated sulphuric acid solution contained higher levels of Pb and Cd. Turan et al. (2004) and Yan et al. (2014) studied metallic residues from a zinc - lead plant and proposed a combination of pyrometallurgical (roasting) and hydrometallurgical (sulphuric acid, water and NaCl) processes for the extraction of Zn and Pb from these residues. Rusan et al. (2008) reported a similar hydrometallurgical extraction process for Zn and brine leaching for Pb extraction from Zn plant residues.

Table 6.4 Different (bio)hydrometallurgical approaches proposed for the leaching of heavy metals from the metallurgical residues

Residue type (metal content – %)	Treatment	Leaching yield	References
Zinc plant residues – Kolwezi zinc plant	Thermal treatment coupled with high concentrated acid leaching	98.7% Zn, 99.9% Cu, and 6.4% Fe obtained after of series of treatment (I. 48% H_2SO_4, II. Thermal treatment at 750 °C for 2 h and III. H_2O leaching at 40 °C)	Ngenda et al. (2009)
Zn – 19.47%			
Cu – 2.7%			
Pb – 2.1%			
Fe – 26.6%			
Zinc plant residues – Kolwezi zinc plant	Acid leaching	More than 90% of Zn and Cd and 80% of Ni extracted at conditions maintained in 1.7 M sulphuric acid concentration, pulp density of 1/8, 400 rpm and 25 °C temperature	Safarzadeh et al. (2009)
Zn – 32.48%			
Cu – 0.075%			
Fe – 0.16%			
Pb – 0.39%			
Zinc plant residues	Combination of pyrometallurgical (roasting) and hydrometallurgical processes (sulphuric acid, water and NaCl)	86% Zn was extracted after roasting at 200 °C for 30 min, 1:1 weight ratio of H_2SO_4: ZPR and leached at 25 °C for 60 min and liquid/solid ratio 20%	Turan et al. (2004)
Zn – 11.3%			
Fe – 8.3%			
Pb – 24.6%			
Neutral leach residue along with zinc ferrite	Series of hydrometallurgical processes including leaching, cementation and refining	80% Zn, 80% Ag and 90% Pb were extracted after series of processes like sulphuric acid leaching (200 g L^{-1} H_2SO_4, 80 °C, 2 h), followed by brine leaching (300 g L^{-1} NaCl, pH 1.5–2.0, 30 min) and by cementation and refining.	Raghavan et al. (1998)
Zinc leach residue	Oxidative leaching and non-oxidative leaching	95% of zinc and 72% of Fe was recovered at pH 1.5, pulp density 1/7, temperature 75 °C and contact time 2 h (non-oxidative leaching)	Alizadeh et al. (2011)
Zn – 9.87%			
Fe – 4.93%			
Zinc leaching residue	Combination of reduction roasting and acid leaching	More than 60% of Zn recovered at 10% of pulp density by 90 g L^{-1} H_2SO_4 at 35 °C and leaching time 1 h	Yan et al. (2014)
Zn – 19.57%			
Fe – 23.91%			
Pb – 4.35%			

(continued)

Table 6.4 (continued)

Residue type (metal content – %)	Treatment	Leaching yield	References
Zinc leach residue 1 (ZLR1)	Acid leaching	More than 90%, 80% and 70% of Zn recovered at 2% of pulp density by 1.5 M H_2SO_4 at 80 °C from ZLR1, ZLR2 and ZLR3, respectively	Sethurajan et al. (2017a)
Zn – 5.01%			
Fe – 6.67%			
Pb – 1.78%			
Zinc leach residue 2 (ZLR2)			
Zn – 2.73%			
Fe – 9.58%			
Pb – 1.53%			
Zinc leach residue 3 (ZLR3)			
Zn – 2.51%			
Fe – 11.5%			
Pb – 2.35%			
Zinc leach residue (ZLR3)	Bioleaching using *A. thiooxidans*	More than 70% of Zn bioleached within 45 days at 2.15% pulp density, 25.1 g L^{-1} external sulphur concentration and initial pH 3.3	Sethurajan et al. (2016b)
Zn – 2.51%			
Fe – 11.5%			
Pb – 2.35%			
Jarosite residue from zinc hydrometallurgy	Hydrometallurgical leaching	More than 95% of Zn, Pb, Cu, Cd and Ag at the end of leaching by NH_4Cl and 94% of As and 73% Si leach residue by 30 wt% NaOH	Ju et al. (2011)
Zn – 8.97%			
Cu – 0.24%			
Fe – 23.1%			
Pb – 4.84%			
Zinc plant residue	Acid leaching	72% of Zn extracted at 20% of pulp density by 150 g L^{-1} H_2SO_4 at 95 °C and leaching time 2 h	Rusen et al. (2008)
Zn – 12.43%			
Fe – 6.27%			
Pb – 15.51%			
Zinc purification residue	Acid leaching	More than 99% of Zn, Cd and Co and 58% of Cu extracted at 25% of pulp density by 48 g L^{-1} H_2SO_4 at 20 °C and leaching time 1 h	Lu et al. (2014)
Zn – 29.1%			
Cu – 24.6%			
Cd – 2.62%			
Co – 0.39%			
Zinc purification residue	Acid leaching	More than 70% of Cu, 60% of Zn and 50% of Cd leached at 2% of pulp density by 1 M H_2SO_4 at 40 °C and within 6 h	Sethurajan et al. (2017b)
Zn – 28.6%			
Cu – 47.2%			
Cd – 9.3%			

6.4 Recovery of Metals from Metallurgical Wastes Leachates

After the leaching of the metals from the metallurgical wastes with acids or microorganisms, the metals are distributed in the leach solution, simply referred to as leachate. Recovery of pure metals from the leachates is extremely important as it is the final and critical stage. Many strategies have been developed for and applied to the extraction of metals from the leachates, with solvent extraction, precipitation, electrowinning and (bio)sorption as the most commonly applied methodologies. Table 6.5 overviews the established metal-recovery strategies. Each of these methods has advantages and disadvantages, so that sometimes a combination of two or three recovery techniques is required to achieve higher metal recovery efficiencies. However, the recovery of metals from metallurgical waste leachates is only in its infancy and requires lots of research and development at laboratory and pilot scale for the development of further commercial applications.

6.4.1 Metal Recovery by Precipitation

Precipitation is a conventional methodology developed for the removal and recovery of metals from metal bearing solutions. Precipitation of metals from metal contaminated aqueous solutions, like acid mine drainage, industrial wastewaters or leaching solutions, can be achieved by the formation of their respective (i) sulphide, (ii) hydroxide, and sometimes (iii) carbonate salts (Manahan 1990). A few metals like arsenic can also be co-precipitated during flocculation with the salts of iron and aluminium. Recovery efficiencies of the metals by precipitation depend highly on the metal concentrations in the solution and also on the system pH. The major disadvantages of precipitation processes are the high requirements of chemicals to adjust the pH and the generation of a not well settling and dewaterable sludge containing toxic compounds (Ahalya et al. 2003).

Metal precipitation occurs when the concentration of ions in solution exceeds the solubility product (Wang et al. 2005), and can be induced by changes in the ionic equilibrium of the system with the addition of the reaction products (either metal or sulphide/hydroxide). Precipitation of metals consists of various stages: (i) nucleation, (ii) growth of nucleus, and (iii) aggregation or crystallisation (Fig. 6.7) (Benning and Waychunas 2008). In some cases, certain chemicals can induce the precipitation (precipitating agents) and subsequent crystal formation (crystallisation nuclei) (Wang et al. 2005).

Table 6.5 Different techniques used for the recovery of metals from metallurgical waste leachates

Source (metal content – g L^{-1})	Treatment	Recovery yield	References
Copper converter flue dust leachates	Solvent Extraction by LIX 860 or MOC-55TD in Iberfluid	More than 70% of Cu recovered	Martin et al. (2003)
Cu – 4.5			
Fe – 1.8			
Zinc plant residues leachates	Solvent extraction by D_2EHPA	More than 90% of indium was recovered from the leachates	Koleini et al. (2010)
Zinc leach residue leachates	Solvent extraction by D_2EHPA	99% of Zn was extracted by 40% of D_2EHPA	Vahidi et al. (2009)
Zn – 28.80			
Pb – 0.011			
Fe – 0.21			
Electric arc furnace dust leachates	Electrowinning	1 kg of pure zinc recovered from the Pb free leachate by using 2.4–2.7 kWh	Youcai and Stanforth (2000)
Zn – 45.60			
Pb – 3.60			
Fe – 0.06			
Cu – 0.06			
Water-jacket furnace flue dusts leachates	Electrowinning	More than 94% of Zn is hydrolysed at the expense of 3.5 kWh/kg energy	Mukongo et al. (2009)
Zn – 35			
Fe – 0.05			
Cu – 0.00013			
Electric arc furnace dust leachates	Electrowinning	92% of Zn was electrolyzed	Tsakiridis et al. (2010)
Zn – 14.0			
Fe – 13.0			
Cu – 0.3			
Copper flue dusts leachates	Electrowinning	88% to 92% of Zn was electrolysed	Qiang et al. (2014)
Zn – 35 – 40			
Pb – 6 – 8			
Al – 0.3 – 0.8			
Cu – 0.2 – 0.5			
EAF dusts leachates	Carbonate precipitation	58% of Zn was precipitated at 10 °C and 700 rpm	Török et al. (2013)
approximately 58			

(continued)

Table 6.5 (continued)

Source (metal content – g L^{-1})	Treatment	Recovery yield	References
EAF dust alkaline leachates	Sulphide precipitation	More than 90% of Zn recovered from the Pb free solution	Youcai and Stanforth (2001)
Leachate 1 – 26.95 of Zn			
Leachate 2 – 45 of Zn			
Leachate 3 – 50.85 of Zn			
Approximately 3 of Pb in all the samples			
EAF dust alkaline leachates	Sulphide precipitation	More than 90% of Zn recovered from the leachates	Lenz and Martins (2007)
Zn – 50			
Pb – 2			
Fe – 0.05			
Zinc leach residue 1 (ZLR1)	Sulphide precipitation	More than 90% of Zn recovered from the leachates at initial pH 4.0 with 100 mg L^{-1} of dissolved sulphide	Sethurajan et al. (2017a)
Zn – 5.01%			
Fe – 6.67%			
Pb – 1.78%			
Zinc leach residue 2 (ZLR2)			
Zn – 2.73%			
Fe – 9.58%			
Pb – 1.53%			
Zinc leach residue 3 (ZLR3)			
Zn – 2.51%			
Fe – 11.5%			
Pb – 2.35%			
Zinc leach residue	Biogenic sulphide precipitation	More than 95% of Zn recovered from the bioleachates at initial pH 5.0 with 1:1 Zn:biogenic sulphide mass ratio.	Sethurajan et al. (2016b)
Zn – 2.51%			
Fe – 11.5%			
Pb – 2.35%			
Zinc purification residue	Sulphide precipitation	More than 95% of Cu recovered from the leachates at initial pH 1.5 with 1:0.5 Cu:sulphide mass ratio.	Sethurajan et al. (2017b)
Zn – 28.6%			
Cu – 47.2%			
Cd – 9.3%			

6.4.1.1 Hydroxide Precipitation

Sodium hydroxide (NaOH) and lime or hydrated lime ($Ca(OH)_2$) are the commonly applied chemicals for the precipitation of metal hydroxides. A generalised equation for the metal hydroxide precipitation can be written as:

$$M^{2+} + 2(OH)^- \leftrightarrow M(OH)_2 \tag{R3}$$

where M is a divalent metal ion.

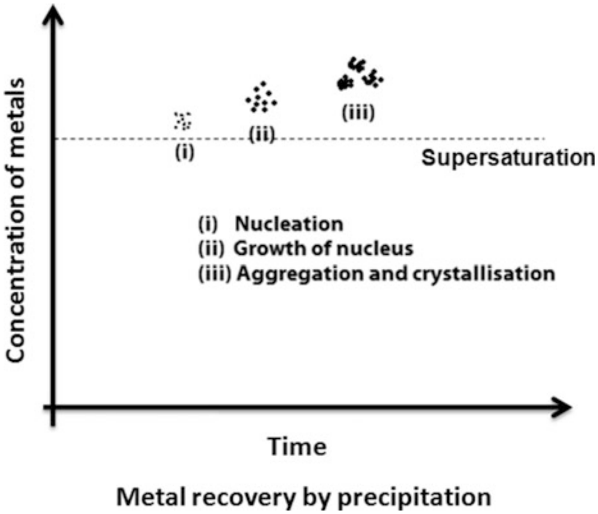
Major disadvantages of this process are non selective recovery of metals and the solubility of the precipitated metal hydroxides: when the pH is not optimal, a soluble metal complex ($M(OH)^+$) will be formed when altering the pH.

6.4.1.2 Carbonate Precipitation

Carbonate precipitation is used to precipitate metals as metal carbonates, in which straight precipitation by chemicals such as calcium carbonate is used or the conversion of hydroxides to carbonates is applied (Wang et al. 2005). Carbonate precipitation can also be applied in combination with hydroxide precipitation.

Varga and Török (2013) studied the precipitation of zinc from EAF dusts ammoniacal leach liquors by using CO_2 (Table 6.5). The tested EAF dusts contained franklinite (49.5%), magnetite (0.5%) and zincite (29%) as the major mineral phases and these dusts were leached by ammonia and ammonium carbonate to dissolve zinc. These leachates and model synthetic solutions were studied for the precipitation of zinc carbonate by using gaseous CO_2. Fifty-eight percent of Zn was precipitated

Fig. 6.7 Various stages in the recovery of metals by precipitation (Benning and Waychunas 2008)



from the leach liquors at 5 L min^{-1}, 700 rpm and 10 °C. The recovery of Zn from synthetic solutions was comparatively poorer (37%) and it was proposed that co-precipitation of Fe and Pb from the leachates might help in enhancing the recovery of Zn from the solutions.

6.4.1.3 Chemical Sulphidic Precipitation

Ferrous sulphide (FeS), calcium sulphide (CaS), sodium sulphide (Na_2S), sodium hydrosulphide (NaHS), ammonium sulphide ($(NH_4)_2S$) and hydrogen sulphide (H_2S) are the major chemicals used for metal sulphide precipitation (MSP). MSP has various advantages over the other precipitation methods, including the fact that metal sulphide precipitates are less soluble, reaction rates are faster, settling properties are better and sulphide precipitates can be combined with ores in metallurgical processes (Lewis 2010). In addition, selective metal recovery by sulfide precipitation is possible with pH or sulfide adjustment (Sampaio et al. 2009, 2010) and can achieve extremely low (ppb range) residual metal concentrations (Kim and Amodeo 1983). The solubility products of different metal sulphides were studied by Sampaio et al. (2009), who found the log K_{SP} values for Cu (I), Cu (II) and Zn (II) to be 48.0, 35.1, and 23.8 respectively. The operational pH (Fig. 6.8) plays an important role in the precipitation of metal sulphides, as various metal

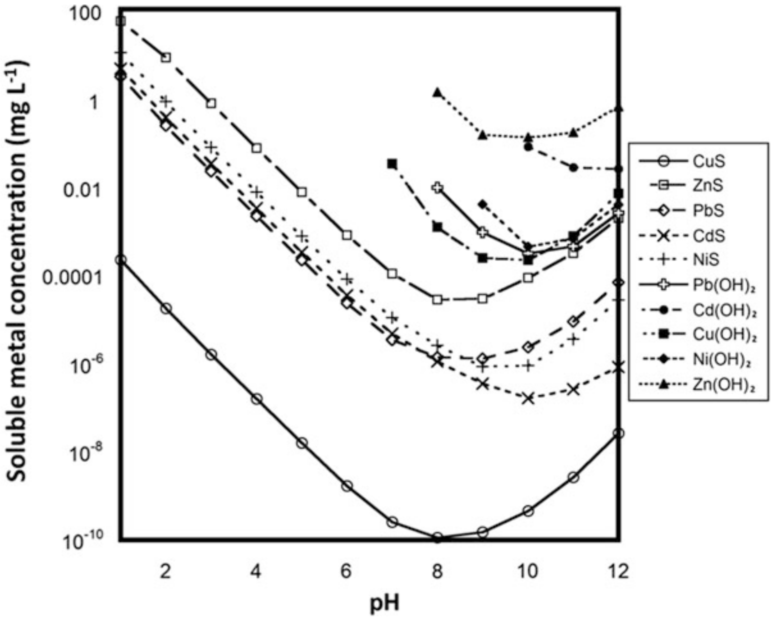


Fig. 6.8 pH dependence of metal sulphide and metal hydroxide solubilities (Resimulated from Lewis 2010 with Visual MINTEQ)

sulphides can solubilise as a function of pH (Lewis 2010). The sulphide concentration is another key factor in MSP (Villa-Gomez et al. 2012); if it is exceeded or depleted either, sulphides or metals will remain in the leachate solution (Veeken et al. 2003).

Metal recovery by MSP has various barriers to cross such as (i) the formation of poly-sulphides owing to the poor mixing of supplied sulphides, which results in excessive consumption of sulphide and low metal recovery, (ii) supersaturation conditions in the solution induced by the low solubility of metal sulphides, which results in the formation of fine particles with poor solid-liquid separation (Lewis and Van Hille 2006) and (iii) formation of impurities like thenardite (Na_2SO_4) limited the selective metal recovery using chemical (Na_2S) sulphide precipitation (Sethurajan et al. 2017a). Lewis and Van Hille (2006) proposed that a gaseous hydrogen sulphide source could decrease the level of supersaturation and thus control the formation of fine particles.

Youcai and Stanforth (2001) investigated the sulphide precipitation of EAF dusts alkaline leachates (Table 6.5), which contained 14.4 g L^{-1} Zn, 2.98 g L^{-1} Pb, 1 g L^{-1} Al, and 0.05 g L^{-1} Fe. These metals were very stable and did not precipitate, even after several months. They proposed that sodium sulphide was a better precipitant than phosphates, sulphates and carbonates. They were able to selectively precipitate lead with a molar ratio of 1.5–1.7 and then the zinc precipitated in the lead free solution. Lenz and Martins (2007) studied the selective chemical precipitation of Pb and Zn (Table 6.5) from EAF dust alkaline leachates. EAF dusts were leached after a series of steps including hydrolysis and alkaline leaching (NaOH). The final leachates contained various metals and the concentrations were 50 g L^{-1} zinc, 2 g L^{-1} lead, 1 g L^{-1} Al and 0.05 g L^{-1} Fe. Sodium sulphide with a 2.0 (w/w) and 3.0 (w/w) weight ratio could achieve almost complete precipitation of Pb in the leachates and later Zn was selectively precipitated by sodium sulphide (in the Pb free solution). Sethurajan et al. (2017a) demonstrated selective sphalerite (ZnS) precipitation from real Zn-leach residue leachates by chemical sulphide precipitation.

6.4.1.4 Biogenic Sulphidic Precipitation

Sulphate reducing bacteria (SRB) are prokaryotes which utilise sulphate and other oxidised sulphur compounds as their terminal electron acceptor (Jorgensen 1982). These anaerobic bacteria have not only assimilatory sulphate reduction (which synthesise sulphur compounds by reducing sulphates), but also dissimilatory sulphate reduction in which the sulphates are reduced to sulphides in the absence of molecular oxygen (Barton and Hamilton 2007). Most of the metal wastes (solid wastes or wastewaters) contain significant amount of sulphates.

SRBs can use simple organic compounds as electron donors and sulphate as the terminal electron acceptor, and produce sulphide which can be used for MSP. The following reactions illustrate the process:

$$\text{Organic matter} + SO_4{}^{2-} \rightarrow H_2S + HCO_3{}^{-} \tag{R4}$$

$$M^{2+} + HS^{-} \rightarrow MS\ (\downarrow) + H^{+} \tag{R5}$$

(M^{2+} – Metal cation)

Metal sulphide precipitation by SRB occurs in two stages: (1) biological hydrogen sulphide production by SRB and (2) metal sulphide precipitation by the biologically produced H_2S. Biological MSP has been reported for the successful recovery of pure metals from various sources like laterite pressure leaching solution (Zhang and Cheng 2007), bioleaching solution from nickel pyrite ore (Cao et al. 2009), industrial wastewater (Kosińska and Miśkiewicz 2012) and Zn leach residue bioleachate (Sethurajan et al. 2016b). The effect of the sulphide concentration and other macro-nutrients on biological MSP (Villa-Gomez et al. 2011, 2012) and the morphological characteristics of the metal sulfides were reported using inversed fluidised bed reactors (Villa-Gomez et al. 2014). The biological MSP technology has been applied at full scale to treat wastewaters containing low metal concentrations (μg – 0.1 g L^{-1}), but not yet to treat metal bearing solid waste leachates (metal concentrations >1 g L^{-1}) at full scale.

6.4.2 Solvent Extraction

Solvent extraction, also referred to as liquid-liquid extraction, requires two liquid phases that are immiscible with each other. The distribution of the solute between the phases greatly depends on the interaction of the solute with the aqueous and organic phases (Choppin and Morgenstern 2000). Solvent extraction has been commercially applied to RLE (Roasting-Leach-Electrowinning technology) liquors. Solvent extraction and electrowinning are often integrated in commercial hydrometallurgical plants to improve the metal recovery efficiency. Prominent developments in the leaching and recovery of metals through solvent extraction and electrowinning were overviewed by Domic (2007). A simplified flow sheet of the unit operations applied in the metallurgical industry (Fig. 6.9a) and a commercial solvent extraction plant are depicted in Fig. 6.9.

Solvent extraction includes three steps to achieve the recovery of pure metals: extraction, stripping and reduction (Fig. 6.10). The major merits of the solvent extraction procedure are: (i) low energy consumption and (ii) regeneration of the solvent.

Solvent extraction has been applied to many waste materials like galvanic sludge (Silva et al. 2005), industrial effluents (Mansur 2011) and fly ashes (Karlfeldt et al.

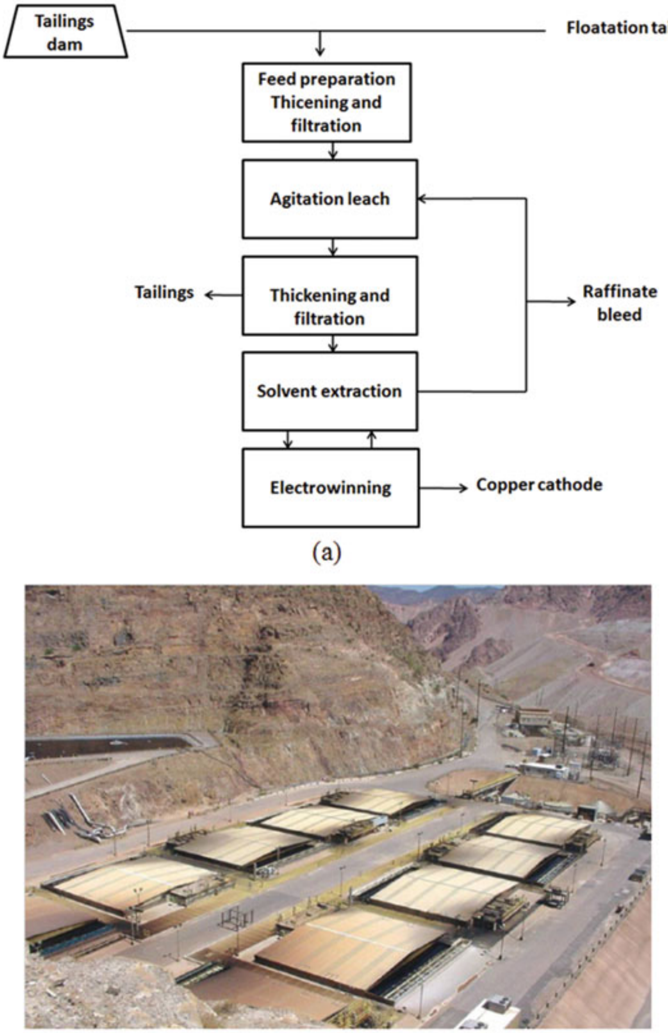


Fig. 6.9 Simplified flow sheet of the leaching and metal recovery by solvent extraction (**a**) electrowinning plant at Konkola Copper Mines, Zambia (Sole et al. 2005) and (**b**) solvent extraction plant Morenci, Arizona, USA (Marsden 2006)

2012) for the extraction of Zn, Cu, In and even for rare earths (Xie et al. 2014). Martín et al. (2003) investigated the extraction of copper from converter flue dust by the combination of acid leaching and solvent extraction procedures (Table 6.5). The dust sample's mineralogical characterisation reveals that it contains 30 wt % of metallic copper (cuprite (Cu_2O), chalcocite ($Cu_{1.96}S$) and 4.5 wt% of Fe (maghemite (γ-Fe_2O_3). Traces of As (0.18 wt %) and Mo (0.09 wt %) were also identified. Sulphuric acid was used as the leachant and a maximum of 2500 ppm of

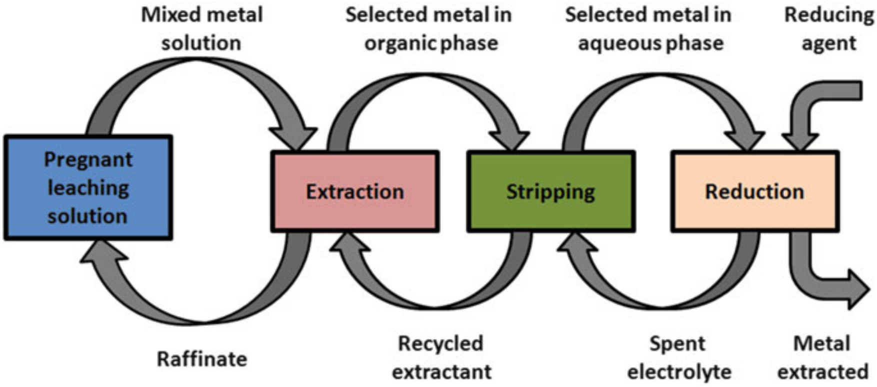


Fig. 6.10 Flow sheet of the recovery of metals by solvent extraction (Redrawn from Wilson et al. 2014)

Cu was leached at 25 °C with 50 g L^{-1} of sulphuric acid. LIX 860 or MOC-55TD was used to recover the Cu from the acidic leachate. These solvents successfully extracted the maximum of metals at the aqueous/organic phase ratio 4.7 at pH 0.5 (Martin et al. Martín et al. 2003).

Vahidi et al. (2009) studied the recovery of zinc by solvent extraction from the roast leach residues by using di-2-ethylhexyl phosphoric acid (D_2EHPA) (Table 6.5). They were able to extract all the zinc from the leach solution with 20% w/w D_2EHPA in the kerosene organic phase (ratio 1:1) at pH 2.5. They found that the addition of tri-butyl phosphate (TBP) (5%) or Na_2SO_4 (0.2 M) enhanced the zinc recovery to the maximum. Interestingly, they found that none of the parameters aqueous organic phase ratio, TBP or Na_2SO_4 concentration had a significant effect on the zinc recovery above pH 2.5 and thus the pH plays a key role in the extraction of Zn by D_2EHPA. Similarly, Koleini et al. (2010) recovered 90% of indium from zinc plant residues using the D_2EHPA solvent-extraction method.

6.4.3 Electrowinning

Electrowinning is applied to recover metals from aqueous solutions. Commercial implementations of electrowinning in combination with solvent extraction are often exploited by the industries. Figure 6.11 shows a commercial electrowinning facility operated at Baghdad (Arizona, USA).

The design of electrowinning processes consists of a chamber, a cathode (negatively charged electrode), an anode (positively charged electrode) and also an electrolyte solution. The mechanism of electrowinning is simple: applying an electric current to the electrolytic solution (eluate), the dissolved positively charged metal ions migrate to and deposit on the negatively charged cathode through the

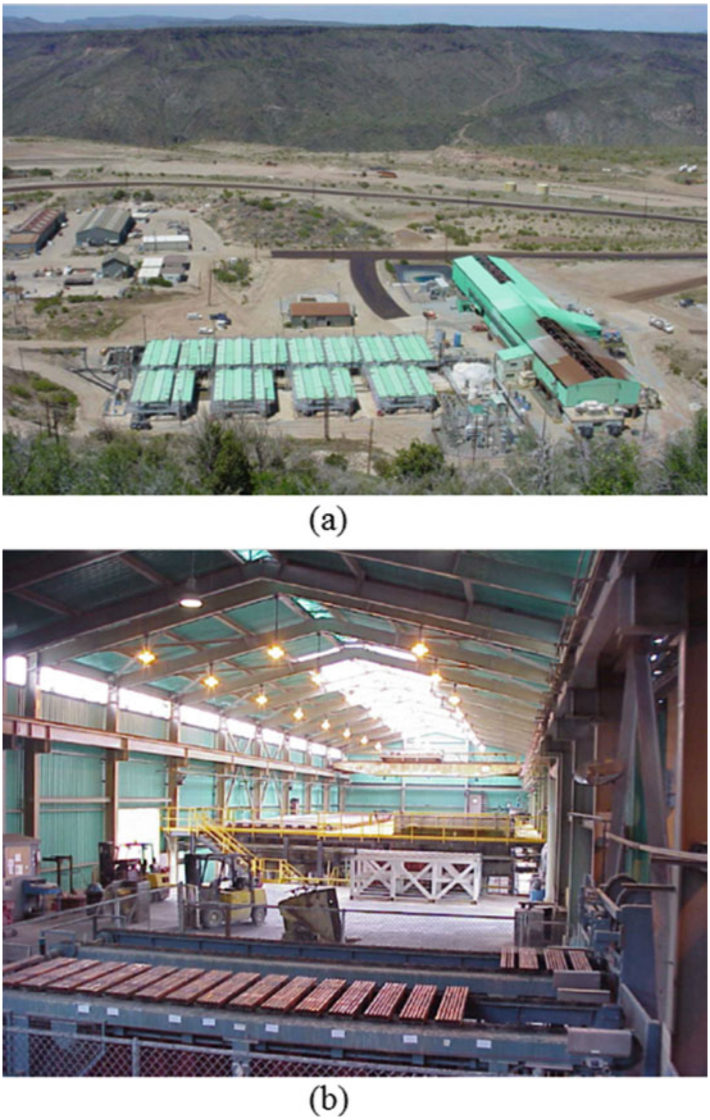


Fig. 6.11 (**a**) Solution-extraction and electrowinning plant and (**b**) Direct copper electrowinning facility at Bagdad (Arizona, USA) (Marsden 2006)

electrons passage to the anode. Unlike the other recovery methods, separation of elemental metal ions is the major advantage of this process. Other highlights of electrowinning processes are no sludge production, no hazardous chemical usage and low capital costs (Kondos et al. 1991). Though electrowinning is a promising recovery technology, recovery of pure metals from multi-metallic solutions is tedious as non-target metals can greatly influence the metal recovery, e.g. copper influences gold extraction (Steyn and Sandenbergh 2004) and lead affects the recovery of zinc (Youcai and Stanforth 2001).

The electrowinning technology was successfully applied to recover metals from leachates of industrial wastes such as electronic scraps and fly ashes (Jha et al. 2001; Vegliò et al. 2003; Cui and Zhang 2008). Electrowinning extraction is more cost effective (especially for the recovery of Zn) in alkaline solutions than in acidic solutions because of their high – energy requirements (St-Pierre and Piron 1986, 1990). Youcai and Stanforth (2000) worked on the separation of pure Zn from an alkaline medium leached EAF dust solution containing Zn 45.60 g L^{-1}, Pb 3.60 g L^{-1}, Fe 0.06 g L^{-1}, Al 1.14 g L^{-1}, Cu 0.06 g L^{-1} and Cd 0.04 g L^{-1} (Table 6.5). The presence of lead in the solution might considerably affect the electrowinning process and Pb was thus pre-removed by sodium sulphide precipitation. The lead depleted solution was used for the electrowinning process to separate pure zinc. 2.4–2.7 kWh electricity was applied to recover 1 kg of pure zinc from the Pb-deprived solution. Mukongo et al. (2009) and Tsakiridis et al. (2010) obtained similar results by applying electrowinning to furnace flue dusts (Table 6.5). They were able to electrolyse more than 90% of Zn from the dust samples at the expense of 3.5 kWh/kg energy.

6.4.4 (Bio)Sorption

Sorption is a widely used and relatively cost-effective metal-recovery technology applied to heavy-metal-containing aqueous solutions. Ion-exchange and expansion properties are important in the selection of suitable sorbent materials. The mechanism of sorption involves three important phases (Das 2010): (i) solid phase (which denotes the sorbent used), (ii) liquid phase (the leachate is usually used as the solvent) and (iii) dissolved phase (refers to the dissolved metal ions). Apart from low cost, sorption has other advantages like low sludge production and multiple use of the sorbent by regeneration of the sorbent. The major limitation of this technique is the early saturation of the (biomass) sorbent (Alluri et al. 2007).

Clay minerals, biological materials, carbon nanotubes, activated carbon, metal oxides and zeolites have been used as sorbents for heavy metals (Zhao et al. 2011). Biological agents such as bacteria, yeasts, fungi and plant materials can also be used in sorption and the process is termed as biosorption. Micro-organisms accumulate metals in the cell wall based on the cell's metabolism and the properties of the cell wall (Fig. 6.12) (Ahalya et al. 2003). In addition, plant tissues are able to accumulate metals, which take up the metals either by active (at the expense of energy) or passive (electrostatic attachment to the cell wall) processes (Fig. 6.12).

Petrisor et al. (2002) reported the biosorption from Romanian mine tailings. Creamer et al. (2006) and Macaskie et al. (2007) demonstrated the use of bacteria (*Desulfovibrio desulfuricans* and *Klebsiella pneumonia*, respectively) to recover

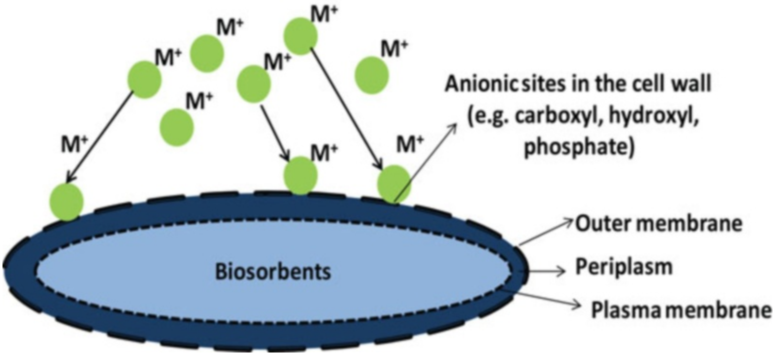


Fig. 6.12 Metal recovery by (bio)sorption

precious metals like gold, silver and palladium from electronic scrap leachates. Zinc removal from leachates of solid industrial waste using hazelnut shell was reported by Turan et al. (2011). Jalili Seh-Bardan et al. (2013) investigated the biosorption of metals such as Zn, Pb, Fe, As and Mn using *Aspergillus fumigates* from gold mine tailing leachates. More rigorous lab scale studies are needed to scale up the biosorption of metals from leachates at large scale levels.

6.5 Conclusions

Huge loads of different metal bearing wastes are produced by different ferrous and non-ferrous metallurgical operations. These metallurgical dusts, sludges, residues and other solid wastes contain high metal concentrations. The two important environmental issues, i.e. growing demand of metals and environmental impacts caused by metallurgical wastes, can be addressed by extraction and recovery of the heavy metals from these wastes. There are different leaching procedures suggested by various authors for distinctly different metal wastes. A variety of metal-recovery strategies have been developed for the successful recovery of metals from the metal containing leachates. Mineralogical phase composition (oxidised or reduced) and metal content play an important role in the selection of suitable leaching and recovery processes. The combination of the knowledge on the mineralogical composition of the waste with the various leaching and metal recovery processes will help to use these metallurgical wastes as potential secondary sources of metals.

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References

Acharya C, Kar RN, Sukla LB (2002) Bioleaching of low grade manganese ore with *Penicillium citrinum*. Eur J Miner Process Environ Prot 2(3):197–204

Ahalya N, Ramachandra TV, Kanamadi RD (2003) Biosorption of heavy metals. Res J Chem Environ 7(4):71–79

Alizadeh R, Rashchi F, Vahidi E (2011) Recovery of zinc from leach residues with minimum iron dissolution using oxidative leaching. Waste Manag Res 29:165–171. doi:10.1177/0734242X10372661

Alluri HK, Ronda SR, Settalluri VS, Bondili JS, Suryanarayana V, Venkateshwar P (2007) Biosorption: an eco-friendly alternative for heavy metal removal. Afr J Biotechnol 6 (25):2924–2931. doi:10.4314/ajb.v6i25.58244

Amiri F, Mousavi SM, Yaghmaei S (2011) Enhancement of bioleaching of a spent Ni/Mo hydroprocessing catalyst by *Penicillium simplicissimum*. Sep Purif Technol 80(3):566–576. doi:10.1016/j.seppur.2011.06.012

Anjum F, Shahid M, Akcil A (2012) Biohydrometallurgy techniques of low grade ores: a review on black shale. Hydrometallurgy 117:1–12. doi:10.1016/j.hydromet.2012.01.007

Asadi-Zeydabadi B, Mowla D, Shariat MH, Fathi Kalajahi J (1997) Zinc recovery from blast furnace flue dust. Hydrometallurgy 47(1):113–125. doi:10.1016/S0304-386X(97)00039-X

Bakhtiari F, Zivdar M, Atashi H, Seyed-Bagheri SA (2008a) Bioleaching of copper from smelter dust in a series of airlift bioreactors. Hydrometallurgy 90(1):40–45. doi:10.1016/j.hydromet.2007.09.010

Bakhtiari F, Atashi H, Zivdar M, Seyed-Bagheri SA (2008b) Continuous copper recovery from a smelter’s dust in stirred tank reactors. Int J Miner Process 86(1–4):50–57

Bakhtiari F, Zivdar M, Atashi H, Seyed-Bagheri S (2010) Continuous bioleaching of copper from copper smelters dust with a mixed culture of mesophilic bacteria. J Chem Soc Pak 32:215–222

Barton LL, Hamilton WA (2007) Sulphate-reducing bacteria: environmental and engineered systems. Cambridge University Press, Cambridge

Bayat O, Sever E, Bayat B, Arslan V, Poole C (2009) Bioleaching of zinc and iron from steel plant waste using *Acidithiobacillus Ferrooxidans*. Appl Biochem Biotechnol 152(1):117–126, https://doi.org/10.1007/s12010-008-8257-5

Benning LG, Waychunas GA (2008) Nucleation, growth, and aggregation of mineral phases: mechanisms and kinetic controls. In: Kinetics of water-rock interaction. Springer, New York, pp 259–333. doi:10.1007/978-0-387-73563-4_7

Bosshard PP, Bachofen R, Brandl H (1996) Metal leaching of fly ash from municipal waste incineration by *Aspergillus niger*. Environ Sci Technol 30:3066–3070. doi:10.1021/es960151v

Brandl H (2001) Microbial leaching of metals. In: Rehm HJ, Reed G (eds) Biotechnology. Wiley-VHC, Weinheim, pp 191–224. doi:10.1002/9783527620999.ch8k

Brierley JA (2008) A perspective on developments in biohydrometallurgy. Hydrometallurgy 94 (1):2–7. doi:10.1016/j.hydromet.2008.05.014

Brierley JA, Brierley CL (1999) Present and future commercial applications of biohydrometallurgy. Process Metallurgy 9:81–89. doi:10.1016/S1572-4409(99)80007-8

Brierley JA, Brierley CL (2001) Present and future commercial applications of biohydrometallurgy. Hydrometallurgy 59(2):233–239. doi:10.1016/S0304-386X(00)00162-6

Brombacher C, Bachofen R, Brandl H (1997) Biohydrometallurgical processing of solids: a patent review. Appl Microbiol Biotechnol 48(5):77–587. doi:10.1007/s002530051099

Burgstaller W, Schinner F (1993) Mini review: leaching of metals with fungi. Biotechnology 27:91–116. doi:10.1016/0168-1656(93)90101-R

Bulut U, Ozverdi A, Erdem M (2009) Leaching behavior of pollutants in ferrochrome arc furnace dust and its stabilization/solidification using ferrous sulphate and Portland cement. J Hazard Mater 162(2-3):893–898

Cantarino MV, de Carvalho-Filho C, Borges-Mansur M (2012) Selective removal of zinc from basic oxygen furnace sludges. Hydrometallurgy 111:124–128. doi:10.1016/j.hydromet.2011.11.004

Cao J, Zhang G, Mao Z, Fang Z, Yang C (2009) Precipitation of valuable metals from bioleaching solution by biogenic sulphides. Miner Eng 22:289–295. doi:10.1016/j.mineng.2008.08.006

Caravaca C, Cobo A, Alguacil FJ (1994) Considerations about the recycling of EAF flue dusts as source for the recovery of valuable metals by hydrometallurgical processes. Resour Conserv Recycl 10:35–41. doi:10.1016/0921-3449(94)90036-1

Chandrappa R, Das DB (2012) Wastes from industrial and commercial activities. In: Solid waste management. Springer, Berlin/Heidelberg, pp 217–247. doi:10.1007/978-3-642-28681-0_9

Chi TD, Lee JC, Pandey BD, Yoo K, Jeong J (2011) Bioleaching of gold and copper from waste mobile phone PCBs by using a cyanogenic bacterium. Miner Eng 30; 24(11): 1219–1222. doi:10.1016/j.mineng.2011.05.009

Choppin GR, Morgenstern A (2000) Thermodynamics of solvent extraction. Solv Extr Ion Exc 18 (6):1029–1049. doi:10.1080/07366290008934721

Cole ER, Dattilo M, O'Keefe TJ (1987) Nonferrous waste as a source of zinc for electrogalvanizing. US Department of the Interior, Bureau of Mines

Creamer NJ, Baxter-Plant VS, Henderson J, Potter M, Macaskie LE (2006) Palladium and gold removal and recovery from precious metal solutions and electronic scrap leachates by *Desulfovibrio desulfuricans*. Biotechnol Lett 28(18):1475–1484. doi:10.1007/s10529-006-9120-9

Cruells M, Roca A, Núñez C (1992) Electric arc furnace flue dusts: characterization and leaching with sulphuric acid. Hydrometallurgy 31(3):213–231. doi:10.1016/0304-386X(92)90119-K

Crundwell FK (2003) How do bacteria interact with minerals? Hydrometallurgy 71:75–81. doi:10.1016/S0304-386X(03)00175-0

Cui JR, Zhang LF (2008) Metallurgical recovery of metals from electronic waste: a review. J Hazard Mater 158:228–256. doi:10.1016/j.jhazmat.2008.02.001

Das N (2010) Recovery of precious metals through biosorption-a review. Hydrometallurgy 103 (1):180–189. doi:10.1016/j.hydromet.2010.03.016

Das B, Prakash S, Reddy PSR, Biswal SK, Mohapatra BK, Misra VN (2002) Effective utilization of blast furnace flue dust of integrated steel plants. Eur J Miner Process Environ Protect 2 (2):61–68

Das B, Prakash S, Reddy PSR, Misra VN (2006) An overview of utilization of slag and sludge from steel industries. Resour Conserv Recycl 50(1):40–57. doi:10.1016/j.resconrec.2006.05.008

Davenport WGL, King M, Schlesinger M, Biswas AK (2002) Extractive metallurgy of copper. Elsevier, Kent

Domic EM (2007) A review of the development and current status of copper bioleaching operations in Chile: 25 years of successful commercial implementation. In: Biomining. Springer, Berlin/Heidelberg, pp 81–95. doi:10.1007/978-3-540-34911-2_4

Dutra AJB, Paiva PRP, Tavares LM (2006) Alkaline leaching of zinc from electric arc furnace steel dust. Miner Eng 19(5):478–485. doi:10.1016/j.mineng.2005.08.013

Duvesteyn WPC, Wicker GR, Doane RE (1979) An omnivorous process for laterite deposits, chapter 28. In: Evans DJI, Shoemaker RS, Veltman H (eds) International laterite Symposium. Society of Mining Engineers of AIME, New York, pp 553–570

Duyvesteyn W, Jha MC (1986) Mixed Lixiviant for separate recovery of zinc and lead from iron-containing materials. US Patent No 4:614, 543

Edwards KJ, Bond PL, Gihring TM, Banfield JF (2000) An archaeal iron-oxidizing extreme acidophile important in acid mine drainage. Science 287:1796–1799. doi:10.1126/science.287.5459.1796

Erdem M, Özverdi A (2011) Environmental risk assessment and stabilization/solidification of zinc extraction residue: II. Stabilization/solidification. Hydrometallurgy 105(3):270–276. doi:10.1016/j.hydromet.2009.10.011

Erust C, Akcil A, Gahan CS, Tuncuk A, Deveci H (2013) Biohydrometallurgy of secondary metal resources: a potential alternative approach for metal recovery. J Chem Technol Biotechnol 88 (12):2115–2132. doi:10.1002/jctb.4164

España JS, Pamo EL, Santofimia E, Aduvire O, Reyes J, Barettino D (2005) Acid mine drainage in the Iberian Pyrite Belt (Odiel river watershed, Huelva, SW Spain): geochemistry, mineralogy and environmental implications. Appl Geochem 20:1320–1356. doi:10.1016/j.apgeochem.2005.01.011

Falco L, Pogliani C, Curutchet G, Donati E (2003) A comparison of bioleaching of covellite using pure cultures of *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* or a mixed culture of *Leptospirillum ferrooxidans* and *Acidithiobacillus thiooxidans*. Hydrometallurgy 71 (1):31–36. doi:10.1016/S0304-386X(03)00170-1

Farbiszewska-Kiczma J, Farbiszewska T, Bąk M (2004) Bioleaching of metals from polish black shale in neutral medium. Physicochem Probl Miner Process 38:273–280

Fu B, Zhou H, Zhang R, Qiu G (2008) Bioleaching of chalcopyrite by pure and mixed cultures of *Acidithiobacillus spp*. and *Leptospirillum ferriphilum*. Int Biodeter Biodegr 62:109–115. doi:10.1016/j.ibiod.2007.06.018

Gabler RC, Jones JR (1988) Metal recovery from secondary copper converter dust by ammoniacal carbonate leaching. US Department of the Interior, Bureau of Mines

Gahan CS, Srichandan H, Kim DJ, Akcil A (2012) Biohydrometallurgy and biomineral processing technology: a review on its past, present and future. Res J Recent Sci 1(10):85–99

Ghosh A, Ray HS (1991) Principles of extractive metallurgy. New Age International, New Delh

Gieré R, Sidenko NV, Lazareva EV (2003) The role of secondary minerals in controlling the migration of arsenic and metals from high sulphide wastes (Berikul gold mine, Siberia). Appl Geochem 18:1347–1359. doi:10.1016/S0883-2927(03)00055-6

Golyshina OV, Pivovarova TA, Karavaiko GI, Kondratéva TF, Moore ER, Abraham WR, Lünsdorf H, Timmis KN, Yakimov MM, Golyshin PN (2000) *Ferroplasma acidiphilum* gen. nov, sp. nov, an acidophilic, autotrophic, ferrous-iron-oxidizing, cell wall- lacking, mesophilic member of the Ferroplasmaceae fam. nov, comprising a distinct lineage of the archaea. Int J Syst Evol Microbiol 50(3):997–1006. doi:10.1099/00207713-50-3-997

Gupta CK (2006) Chemical metallurgy: principles and practice. Wiley, Weinheim

Hammarstrom JM, Seal RR II, Meier AL, Kornfeld JM (2005) Secondary sulphate minerals associated with acid drainage in the eastern US: recycling of metals and acidity in surficial environments. Chem Geol 215:407–431. doi:10.1016/j.chemgeo.2004.06.053

Han Y, Ma X, Zhao W, Chang Y, Zhang X, Wang X, Huang Z (2013) Sulphur-oxidizing bacteria dominate the microbial diversity shift during the pyrite and low-grade pyrolusite bioleaching process. J Biosci Bioeng 116(4):465–471. doi:10.1016/j.jbiosc.2013.04.012

Havlik T, Friedrich B, Stopic S (2004) Pressure leaching of EAF dust with sulphuric acid. Erzmetall 57(2):83–90

Havlík T, Bernardes AM, Schneider IAH, Miškufová A (2006) Hydrometallurgical processing of carbon steel EAF dust. J Hazard Mater 135(1):311–318. doi:10.1016/j.jhazmat.2005.11.067

Henry A (1997) Schnell, Bioleaching of Copper, Biomining, Biotechnology Intelligence Unit, pp 21–43

Hita R, Torrent J, Bigham JM (2006) Experimental oxidative dissolution of sphalerite in the Aznalcóllar sludge and other pyrite matrices. J Environ Qual 35:1032–1039. doi:10.2134/jeq2005.0371

Hita R, Wang H, Bigham JM, Torrent J, Tuovinen OH (2008) Bioleaching of a pyritic sludge from the Aznalcóllar (Spain) mine spillage at ambient and elevated temperatures. Hydrometallurgy 93(1):76–79. doi:10.1016/j.hydromet.2008.03.004

Ilyas S, Chi RA, Lee JC (2013) Fungal bioleaching of metals from mine tailing. Miner Process Extr M 34(3):185–194. doi:10.1080/08827508.2011.623751

Işıldar A, van de Vossenberg J, Rene ER, van Hullebusch ED, Lens PNL (2016) Two-step bioleaching of copper and gold from discarded printed circuit boards (PCB). Waste Manag 57:149–157. doi:10.1016/j.wasman.2015.11.033

Jalili Seh-Bardan B, Othman R, Abd-Wahid S, Sadegh-Zadeh F, Husin A (2013) Biosorption of heavy metals in leachate derived from gold mine tailings using *Aspergillus fumigatus*. CLEAN Soil Air Water 41(4):356–364. doi:10.1002/clen.201200140

Jha MK, Kumar V, Singh RJ (2001) Review of hydrometallurgical recovery of zinc from industrial wastes. Resour Conserv Recycl 33:1–22. doi:10.1016/S0921-3449(00)00095-1

Johnson DB (2006) Biohydrometallurgy and the environment: intimate and important interplay. Hydrometallurgy 83:153–166. doi:10.1016/j.hydromet.2006.03.051

Johnson DB (2009) Extremophiles: acid environments. In: Schaechter M (ed) Encyclopedia of microbiology. Elsevier, Oxford, pp 107–126

Johnson DB (2013) Development and application of biotechnologies in the metal mining industry. Environ Sci Pollut Res Int 20(11):7768–7776. doi:10.1007/s11356-013-1482-7

Johnson DB (2014) Biomining - biotechnologies for extracting and recovering metals from ores and waste materials. Curr Opin Biotechnol 30:24–31. doi:10.1016/j.copbio.2014.04.008

Johnson DB, Grail BM, Hallberg KB (2013) A new direction for biomining: extraction of metals by reductive dissolution of oxidized ores. Fortschr Mineral 3(1):49–58. doi:10.3390/min3010049

Jorgensen BB (1982) Ecology of the bacteria of the sulphur cycle with special reference to anoxic-oxic interface environments. Philos Trans R Soc Lond B 298:543–561. doi:10.1098/rstb.1982.0096

Ju S, Zhang Y, Zhang Y, Xue P, Wang Y (2011) Clean hydrometallurgical route to recover zinc, silver, lead, copper, cadmium and iron from hazardous jarosite residues produced during zinc hydrometallurgy. J Hazard Mater 192(2):554–558. doi:10.1016/j.jhazmat.2011.05.049

Kachur AN, Arzhanova VS, Yelpatyevsky PV, von Braun MC, von Lindern IH (2003) Environmental conditions in the Rudnaya River watershed – a compilation of Soviet and post- Soviet era sampling around a lead smelter in the Russian Far East. Sci Total Environ 303:171–185. doi:10.1016/S0048-9697(02)00351-0

Kaksonen AH, Mudunuru BM, Hackl R (2014) The role of microorganisms in gold processing and recovery – a review. Hydrometallurgy 142:70–83. doi:10.1016/j.hydromet.2013.11.008

Karlfeldt FK, Ekberg C, Skarnemark G, Steenari B-M (2012) Initial studies on the recovery of Cu from MSWI fly ash leachates using solvent extraction. Waste Manag Res 30:1072–1080. doi:10.1177/0734242X12441385

Ke Y, Chai LY, Min XB, Tang CJ, Chen J, Wang Y, Liang YJ (2014) Sulphidation of heavy-metal-containing neutralization sludge using zinc leaching residue as the sulphur source for metal recovery and stabilization. Miner Eng 61:105–112. doi:10.1016/j.mineng.2014.03.022

Keith DC, Runnells DD, Esposito KJ, Chermak JA, Levy DB, Hannula SR, Watts M, Hall L (2001) Geochemical models of the impact of acidic groundwater and evaporative sulphate salts on Boulder Creek at Iron Mountain, California. Appl Geochem 16:947–961. doi:10.1016/S0883-2927(00)00080-9

Kelebek S, Yörük S, Davis B (2004) Characterization of basic oxygen furnace dust and zinc removal by acid leaching. Miner Eng 17(2):285–291. doi:10.1016/j.mineng.2003.10.030

Kelly DP, Wood AP (2000) Reclassification of some species of *Thiobacillus* to the newly designated genera *Acidithiobacillus* gen. nov, *Halothiobacillus* gen. nov. and *Thermithiobacillus* gen. nov. Int J Syst Evol Microbiol 50:511–516. doi:10.1099/00207713-50-2-511

Kierczak J, Néel C, Puziewicz J, Bril H (2009) The mineralogy and weathering of slag produced by the smelting of lateritic Ni ores, Szklary, southwestern Poland. Can Mineral 47:557–572. doi:10.3749/canmin.47.3.557

Kim BM, Amodeo PA (1983) Calcium sulfide process for treatment of metal containing wastes. Environ Prog 2(3):175–180. doi:10.1002/ep.670020309

Koleini SM, Mehrpouya H, Saberyan K, Abdolahi M (2010) Extraction of indium from zinc plant residues. Miner Eng 23(1):51–53. doi:10.1016/j.mineng.2009.09.007

Kondos PD, Mackinnon DJ, Mccready RGL, Riveros PA, Skaff M (1991) Study on metals recovery/recycling from acid mine drainage phase ia: literature survey, 1–47. http://mend-nedem.org/wp-content/uploads/(2013)/01/3.21.1a.pdf

Kosińska K, Miśkiewicz T (2012) Precipitation of heavy metals from industrial wastewater by *Desulfovibrio desulfuricans*. Environ Prot Eng 38(2):51–60. doi:10.5277/epe120205

Laforest G, Duchesne J (2006) Characterization and leachability of electric arc furnace dust made from remelting of stainless steel. J Hazard Mater 135(1):156–164. doi:10.1016/j.jhazmat.2005.11.037

Lee JC, Pandey BD (2012) Bio-processing of solid wastes and secondary resources for metal extraction – a review. Waste Manag 32:3–18. doi:10.1016/j.wasman.2011.08.010

Lenz DM, Martins FB (2007) Lead and zinc selective precipitation from leach electric arc furnace dust solutions. Revista Matéria 12(3):503–509. http://dx.doi.org/10.1590/S1517-70762007000300011

Leonard RP (1978) Hazardous solid waste from metallurgical industries. Environ Health Perspect 27:251–260

Lewis AE (2010) Review of metal sulphide precipitation. Hydrometallurgy 104:222–234. doi:10.1016/j.hydromet.2010.06.010

Lewis A, van Hille R (2006) An exploration into the sulphide precipitation method and its effect on metal sulphide removal. Hydrometallurgy 81(3):197–204. doi:10.1016/j.hydromet.2005.12.009

Li M, Peng B, Chai LY, Peng N, Xie XD, Yan H (2013) Technological mineralogy and environmental activity of zinc leaching residue from zinc hydrometallurgical process. T Nonferr Metal Soc 23(5):1480–1488. doi:10.1016/S1003-6326(13)62620-5

Lingling L, Lu Z, Weiwei J (2012) Screening and identification of *Pseudomonas aeruginosa* LLJQ-1 and its role in bioleaching of low-grade collophanite. In: World Automation Congress (WAC), 1–6. IEEE

Lottermoser BG (2010) Mine wastes: characterization, treatment, and environmental impacts. Springer, Berlin

Lu D, Jin Z, Shi L, Tu G, Xie F, Asselin E (2014) A novel separation process for detoxifying cadmium-containing residues from zinc purification plants. Miner Eng 64:1–6. doi:10.1016/j.mineng.2014.03.026

Macaskie LE, Creamer NJ, Essa AMM, Brown NL (2007) A new approach for the recovery of precious metals from solution and from leachates derived from electronic scrap. Biotechnol Bioeng 96(4):631–639. doi:10.1002/bit.21108

Malhotra D, Taylor P, Spiller E, LeVier M (2009) Recent advances in mineral processing plant design. SME, Colorado

Manahan SE (1990) Hazardous waste chemistry, toxicology, and treatment. CRC Press, Boca Raton

Mansfeldt T, Dohrmann R (2004) Chemical and mineralogical characterization of blast-furnace sludge from an abandoned landfill. Environ Sci Technol 38(22):5977–5984. doi:10.1021/es040002

Mansur MB (2011) Solvent extraction for metal and water recovery from industrial wastes and effluents. R Esc Minas 64(1):51–55. http://dx.doi.org/10.1590/S0370-44672011000100006

Marsden JO (2006) Recent developments in copper hydrometallurgy. In: Sohn international symposium; advanced processing of metals and materials, Volume 1: Thermo and physico-chemical principles: non-ferrous high-temperature processing, Vol 1, pp 833–834

Martín IM, López-Delgado A, López FA, Coedo AG, Dorado MT, Alguacil FJ (2003) Treatment of copper converter flue dust for the separation of metallic/non-metallic copper by hydrometallurgical processing. J Chem Eng Japan 36(12):1498–1502. doi:10.1252/jcej.36.1498

Massianaie M, Oliazadeh M, Bagheri AS (2006) Biological copper extraction from melting furnace dust of Sarcheshmeh copper mine. Int J Miner Process 81:58–62. doi:10.1016/j.minpro.2006.06.005

Min XB, Xie XD, Chai LY, Liang YJ, Li M, Ke Y (2013) Environmental availability and ecological risk assessment of heavy metals in zinc leaching residue. T Nonferr Metal Soc 23(1):208–218. doi:10.1016/S1003-6326(13)62448-6

Mukongo T, Maweja K, Mutombo I, Tshilombo K (2009) Zinc recovery from the water-jacket furnace flue dusts by leaching and electrowinning in a SEC-CCS cell. Hydrometallurgy 97(1):53–60. doi:10.1016/j.hydromet.2009.01.001

Müller B, Burgstaller W, Strasser H, Zanella A, Schinner F (1995) Leaching of zinc from an industrial filter dust with *Penicillium, Pseudomonas* and *Corynebacterium*: Citric acid is the leaching agent rather than amino acids. J Ind Microbiol 14(3–4):208–212. doi:10.1007/BF01569929

Mulligan CN, Galvez-Cloutier R, Renaud N (1999) Biological leaching of copper mine residues by *Aspergillus niger*. Process Metallurgy 9:453–461. doi:10.1016/S1572-4409(99)80046-7

Mulligan CN, Kamali M, Gibbs BF (2004) Bioleaching of heavy metals from a low-grade mining ore using *Aspergillus niger*. J Hazard Mater 110(1):77–84. doi:10.1016/j.jhazmat.2004.02.040

National Research Council (US) (2002) Committee on technologies for the mining industries. In: Evolutionary and revolutionary technologies for mining. National Academy Press, Washington, DC

Neale JW, Gericke M, Ramcharan K (2011) The application of bioleaching to base metal sulphides in southern Africa: prospects and opportunities. In: The Southern African Institute of Mining and Metallurgy 6th Southern African Base Metals Conference, pp 367–388. doi: 10.13140/2.1.2461.6323

Ngenda RB, Segers L, Kongolo PK (2009) Base metals recovery from zinc hydrometallurgical plant residues by digestion method. Hydrometallurgy Conference, The Southern African Institute of Mining and Metallurgy, pp 17–29

Norris PR, Burton NP, Foulis NAM (2000) Acidophiles in bioreactor mineral processing. Extremophiles 4:71–76. doi:10.1007/s007920050139

Nouren S, Bhatti HN, Ilyas S (2011) Bioleaching of copper, aluminium, magnesium and manganese from brown shale by *Ganoderma lucidum*. Afr J Biotechnol 10:10664–10673. doi:10.5897/AJB11.1380

Oliazadeh M, Massianaie M, Bagheri AS, Shahverdi AR (2006) Recovery of copper from melting furnaces dust by microorganisms. Miner Eng 19:209–210. doi:10.1016/j.mineng.2005.09.004

Olson GJ, Brierley JA, Brierley CL (2003) Bioleaching review (Part B): processing in bioleaching: applications of microbial processes by the minerals industries. Appl Microbiol Biotechnol 63:249–257. doi:10.1007/s00253-003-1404-6

Pearson D (1981) Recovery of zinc from metallurgical dusts and fumes, process and fundamental considerations of selected hydrometallurgical systems. In: Kuhn MC (ed) Chapter 14. Society of Mining Engineers of AIME, New York, pp 153–168

Pereira CF, Rodrıguez-Piñero M, Vale J (2001) Solidification/stabilization of electric arc furnace dust using coal fly ash: analysis of the stabilization process. J Hazard Mater 82(2):183–195. doi:10.1016/S0304-3894(00)00359-9

Petrisor IG, Komnitsas K, Lazar I, Voicu A, Dobrota S, Stefanescu M (2002) Biosorption of heavy metals from leachates generated at mine waste disposal sites. Eur J Miner Process Environ Prot 2(3):158–167

Plumb JJ, Muddle R, Franzmann PD (2008) Effect of pH on rates of iron and sulphur oxidation by bioleaching organisms. Miner Eng 21:76–82. doi:10.1016/j.mineng.2007.08.018

Pradhan JK, Kumar S (2012) Metals bioleaching from electronic waste by *Chromobacterium violaceum* and *Pseudomonads* sp. Waste Manag Res 30(11):1151–1159. doi:10.1177/0734242X12437565

Qiang L, Pinto IS, Youcai Z (2014) Sequential stepwise recovery of selected metals from flue dusts of secondary copper smelting. J Clean Prod 84:663–670. doi:10.1016/j.jclepro.2014.03.085

Raghavan R, Mohanan PK, Patnaik SC (1998) Innovative processing technique to produce zinc concentrate from zinc production residue with simultaneous recovery of lead and silver. Hydrometallurgy 48(2):225–237. doi:10.1016/S0304-386X(97)00082-0

Rao SR (2011) Resource recovery and recycling from metallurgical wastes. In: Waste management series. Elsevier Science, The Netherlands

Rao DV, Shivannavar CT, Gaddad SM (2002) Bioleaching of copper from chalcopyrite ore by fungi. Indian J Exp Biol 40(3):319–324

Rawlings DE (2005) Characteristics and adaptability of iron- and sulphur-oxidizing microorganisms used for the recovery of metals from minerals and their concentrates. Microb Cell Factories 4:1–15. doi:10.1186/1475-2859-4-13

Renman R, Jiankang W, Jinghe C (2006) Bacterial heap-leaching: practice in Zijinshan copper mine. Hydrometallurgy 83(1):77–82. doi:10.1016/j.hydromet.2006.03.048

Reuter M, Lans S, Booster J (1998) Zinc. Course notes for Zinc College (1999) Report Department of Raw Materials Technology, Delft University of Technology, The Netherlands, pp 1–50

Riekkola-Vanhanen M (2010) Talvivaara Sotkamo mine - bioleaching of a polymetallic nickel ore in subarctic climate. Nova Biotechnol 10(1):7–13

Romero A, González I, Galán E (2006) The role of efflorescent sulphates in the storage of trace elements in stream waters polluted by acid mine-drainage: the case of Peña Del Hierro, Southwestern Spain. Can Mineral 44:1431–1446. doi:10.2113/gscanmin.44.6.1431

Rossi G (1990) Biohydrometallurgy. McGraw-Hill, Hamburg

Ruşen A, Sunkar AS, Topkaya YA (2008) Zinc and lead extraction from Çinkur leach residues by using hydrometallurgical method. Hydrometallurgy 93(1):45–50. doi:10.1016/j.hydromet.2008.02.018

Safarzadeh MS, Moradkhani D, Ojaghi-Ilkhchi M (2009) Kinetics of sulphuric acid leaching of cadmium from Cd-Ni zinc plant residues. J Hazard Mater 163(2):880–890. doi:10.1016/j.jhazmat.2008.07.082

Safarzadeh MS, Dhawan N, Birinci MD, Moradhani D (2011) Reductive leaching of cobalt from zinc plant purification residues. Hydrometallurgy 106:51–57. doi:10.1016/j.hydromet.2010.11.017

Salihoglu G, Pinarli V (2008) Steel foundry electric arc furnace dust management: stabilization by using lime and Portland cement. J Hazard Mater 153(3):1110–1116. doi:10.1016/j.jhazmat.2007.09.066

Sampaio RMM, Timmers RA, Xu Y, Keesman KJ, Lens PNL (2009) Selective precipitation of Cu from Zn in a pS controlled continuously stirred tank reactor. J Hazard Mater 165(1):256–265. doi:10.1016/j.jhazmat.2008.09.117

Sampaio RMM, Timmers RA, Kocks N, André V, Duarte MT, van Hullebusch ED, Lens PNL (2010) Zn-Ni sulphide selective precipitation: the role of supersaturation. Sep Purif Technol 74(1):108–118. doi:10.1016/j.seppur.2010.05.013

Sánchez-España J, López-Pamo E, Santofimia E, Aduvire O, Reyes J, Barettino D (2005) Acid mine drainage in the Iberian Pyrite Belt (Odiel river watershed, Huelva, SW Spain): geochemistry, mineralogy and environmental implications. Appl Geochem 20(7):1320–1356. doi:10.1016/j.apgeochem.2005.01.011

Sand W, Rohde K, Sobotke B, Zenneck C (1992) Evaluation of *Leptospirillum ferrooxidans* for leaching. Appl Environ Microbiol 58(1):85–92

Sandstrom A, Petersson S (1997) Bioleaching of a complex sulphide ore with moderate thermophilic and extreme thermophilic microorganisms. Hydrometallurgy 46:181–190. doi:10.1016/S0304-386X(97)00012-1

Schinner F, Burgstaller W (1989) Extraction of zinc from industrial waste by *Penicillium* sp. Appl Environ Microbiol 55:1153–1156

Sethurajan M, Aruliah R, Karthikeyan OP, Balasubramanian R (2012) Bioleaching of copper from black shale ore using mesophilic mixed populations in an air up-lift bioreactor. Environ Eng Manag J 11(10):1839–1848

Sethurajan M, Huguenot D, Horn HA, Figueiredo LAF, Lens PNL, van Hullebusch ED (2016a) Fractionation and leachability of heavy metals from aged and recent Zn-metallurgical leach residues from the Três Maris Zinc plant (MG, Brazil). Environ Sci Pollut R 23(8):7504–7516. doi:10.1007/s11356-015-6014-1

Sethurajan M, Huguenot D, Horn HA, Figueiredo LAF, Lens PNL, van Hullebusch ED (2016b) Selective recovery of copper from hazardous zinc hydrometallurgical purification residues. J Environ Manag 177:26–35. doi:10.1016/j.jenvman.2016.03.041

Sethurajan M, Huguenot D, Jain R, Horn HA, Figueiredo LAF, Lens PNL, van Hullebusch ED (2017a) Leaching and selective zinc recovery from acidic leachates of zinc metallurgical leach residues. J Hazard Mater 324:71–82. doi:10.1016/j.jhazmat.2016.01.028

Sethurajan M, Lens PNL, Rene ER, van de Vossenberg J, Huguenot D, Horn HA, Figueiredo LAF, van Hullebusch ED (2017b) Bioleaching and selective biorecovery of zinc from zinc metallurgical leach residues from the Três Marias zinc plant (Minas Gerais, Brazil). J Chem Technol Biotechnol 92(3):512–521. doi:10.1002/jctb.5026

Shen H, Forssberg E (2003) An overview of recovery of metals from slags. Waste Manag 23 (10):933–949. doi:10.1016/S0956-053X(02)00164-2

Silva JE, Paiva AP, Soares D, Labrincha A, Castro F (2005) Solvent extraction applied to the recovery of heavy metals from galvanic sludge. J Hazard Mater 120:113–118. doi:10.1016/j.jhazmat.2004.12.008

Sole KC, Feather AM, Cole PM (2005) Solvent extraction in southern Africa: an update of some recent hydrometallurgical developments. Hydrometallurgy 78(1):52–78. doi:10.1016/j.hydromet.2004.11.012

Solisio C, Lodi A, Veglio F (2002) Bioleaching of zinc and aluminium from industrial waste sludges by means of *Thiobacillus ferrooxidans*. Waste Manag 22:667–675. doi:10.1016/S0956-053X(01)00052-6

Steyn J, Sandenbergh RF (2004) A study of the influence of copper on the gold electrowinning process. J S Afr I Min Metall 104(3):177–182

St-Pierre J, Piron DL (1986) Electrowinning of zinc from alkaline solutions. J Appl Electrochem 16(3):447–456. doi:10.1007/BF01008856

St-Pierre J, Piron DL (1990) Electrowinning of zinc from alkaline solutions at high current densities. J Appl Electrochem 20(1):163–165. doi:10.1007/BF01012487

Sukla LB, Panchanadikar V (1993) Bioleaching of lateritic nickel ore using a heterotrophic microorganism. Hydrometallurgy 32(3):373–379. doi:10.1016/0304-386X(93)90048-I

Sukla LB, Kar RN, Panchanadikar VV, Choudhury S, Mishra RK (1995) Bioleaching of lateritic nickel ore using *Penicillium* sp. Trans Indian Inst Met (India) 48(2):103–106

Terézia V, Tamási T (2013) Experimental investigation of zinc precipitation from eaf dust leaching solutions. Mater Sci Eng 38(1):61–71

Török T (2013) Experimental investigation of zinc precipitation from EAF dust leaching solutions. Mater Sci Eng 38(1):61–71

Trefry JH, Metz S (1984) Selective leaching of trace metals from sediments as a function of pH. Anal Chem 56(4):745–749. doi:10.1021/ac00268a034

Trung ZH, Kukurugya F, Takacova Z, Orac D, Laubertova M, Miskufova A, Havlik T (2011) Acidic leaching both of zinc and iron from basic oxygen furnace sludge. J Hazard Mater 192 (3):1100–1107. doi:10.1016/j.jhazmat.2011.06.016

Tsakiridis PE, Oustadakis P, Katsiapi A, Agatzini-Leonardou S (2010) Hydrometallurgical process for zinc recovery from electric arc furnace dust (EAFD). Part II: Downstream processing and zinc recovery by electrowinning. J Hazard Mater 179(1):8–14. doi:10.1016/j.jhazmat.2010.01.059

Turan MD, Altundoğan HS, Tümen F (2004) Recovery of zinc and lead from zinc plant residue. Hydrometallurgy 75(1–4):169–176. doi:10.1016/j.hydromet.2004.07.008

Turan NG, Mesci B, Ozgonenel O (n.d.2011) Artificial neural network (ANN) approach for modelling Zn (II) adsorption from leachate using a new biosorbent. Chem Eng J 173 (1):98–105. doi: 10.1016/j.cej.2011.07.042

Tutor FV, Murciego AM, Valle PA, Ayuso EÁ, Pascual EP, Sánchez AG (2013) Weathering products of arsenopyrite and pyrite from El Bollo mine wastes (Salamanca, Spain) and their environmental hazards. Revista De La Sociedad Española De Mineralogía:111–112

Upadhyay SN (2002) Mineral biotechnology: potential and problems. In: Sukla LB, Misra VN (eds) Proceedings of the national seminar on mineral biotechnology. Allied Publishers Pvt Ltd, India, pp 16–31

Uroz S, Calvaruso C, Turpault MP, Frey-Klett P (2009) Mineral weathering by bacteria: ecology, actors and mechanisms. Trends Biotechnol 17(8):378–387. doi:10.1016/j.tim.2009.05.004

Vahidi E, Rashchi F, Moradkhani D (2009) Recovery of zinc from an industrial zinc leach residue by solvent extraction using D2EHPA. Miner Eng 22(2):204–206. doi:10.1016/j.mineng.2008.05.002

Vakylabad AB (2011) A comparison of bioleaching ability of mesophilic and moderately thermophilic culture on copper bioleaching from flotation concentrate and smelter dust. Int J Miner Process 101(1-4):94–99

Vakylabad AB, Schaffie M, Ranjbar M, Manafi Z, Darezereshki E (2012) Bio-processing of copper from combined smelter dust and flotation concentrate: a comparative study on the stirred tank and airlift reactors. J Hazard Mater 241–242:197–206. doi:10.1016/j.jhazmat.2012.09.031

Van Herck P, Vandecasteele C (2000) Zinc and lead removal from blast furnace sludge with a hydrometallurgical process. Environ Sci Technol 34(17):3802–3808. doi:10.1021/es991033l

Veeken AHM, Akoto L, Hulshoff-Pol LW, Weijma J (2003) Control of the sulfide (S^{2-}) concentration for optimal zinc removal by sulfide precipitation in a continuously stirred tank reactor. Water Res 37(15):3709–3717. doi:10.1016/S0043-1354(03)00262-8

Veglio F, Quaresima R, Fornari P (2003) Recovery of valuable metals from electronic and galvanic industrial wastes by leaching and electrowinning. Waste Manag 23(3):245–252. doi:10.1016/S0956-053X(02)00157-5

Vereš J, Lovás M, Jakabský Š, Šepelák V, Hredzák S (2012) Characterization of blast furnace sludge and removal of zinc by microwave assisted extraction. Hydrometallurgy 129:67–73. doi:10.1016/j.hydromet.2012.09.008

Vestola EA, Kusenaho MA, Narhi HM, Touvinen OH, Puhakka JA, Plumb JJ, Kaksonen AH (2010) Acid bioleaching of solid waste materials from copper, steel and recycling industries. Hydrometallurgy 103:74–79. doi:10.1016/j.hydromet.2010.02.017

Villa-Gomez DK, Ababneh H, Papirio S, Rousseau DPL, Lens PNL (2011) Effect of sulphide concentration on the location of the metal precipitates in inversed fluidized bed reactors. J Hazard Mater 192:200–207. doi:10.1016/j.jhazmat.2011.05.002

Villa-Gomez DK, Papirio S, van Hullebusch ED, Farges F, Nikitenko S, Kramer H, Lens PNL (2012) Influence of sulphide concentration and macronutrients on the characteristics of metal precipitates relevant to metal recovery in bioreactors. Bioresour Technol 110:26–34. doi:10.1016/j.biortech.2012.01.041

Villa-Gomez DK, van Hullebusch ED, Maestro R, Farges F, Nikitenko S, Kramer H, Lens PNL (2014) Morphology, mineralogy, and solid-liquid phase separation characteristics of Cu and Zn precipitates produced with biogenic sulphide. Environ Sci Technol 48(1):664–673. doi:10.1021/es402795x

Vítková M, Ettler V, Hyks J, Astrup T, Kříbek B (2011) Leaching of metals from copper smelter flue dust (Mufulira, Zambian copper belt). Appl Geochem 26:S263–S266. doi:10.1016/j.apgeochem.2011.03.120

Wang LK, Hung YT, Shammas NK (2005) Physicochemical treatment processes, Col 3. Springer, Humana Press, Totowa

Watling HR (2006) The bioleaching of sulphide minerals with emphasis on copper sulphides - a review. Hydrometallurgy 84:81–108. doi:10.1016/j.hydromet.2006.05.001

Wilson AM, Bailey PJ, Tasker PA, Turkington JR, Grant RA, Love JB (2014) Solvent extraction: the coordination chemistry behind extractive metallurgy. Chem Soc Rev 43(1):123–134. doi:10.1039/c3cs60275c

Wong MH (1986) Reclamation of wastes contaminated by copper, lead, and zinc. Environ Manag 10(6):707–713. doi:10.1007/BF01867725

Wu HY, Ting YP (2006) Metal extraction from municipal solid waste (MSW) incinerator fly ash-Chemical leaching and fungal bioleaching. Enz Microbial Technol 38:839–847. doi:10.1016/j.enzmictec.2005.08.012

Xia DK, Picklesi CA (2000) Microwave caustic leaching of electric arc furnace dust. Miner Eng 13 (1):79–94. doi:10.1016/S0892-6875(99)00151-X

Xie F, Zhang TA, Dreisinger D, Doyle F (2014) A critical review on solvent extraction of rare earths from aqueous solutions. Miner Eng 56:10–28. doi:10.1016/j.mineng.2013.10.021

Yan H, Chai LY, Peng B, Li M, Peng N, Hou DK (2014) A novel method to recover zinc and iron from zinc leaching residue. Miner Eng 55:103–110. doi:10.1016/j.mineng.2013.09.015

Youcai Z, Stanforth R (2000) Integrated hydrometallurgical process for production of zinc from electric arc furnace dust in alkaline medium. J Hazard Mater 80(1):223–240. doi:10.1016/S0304-3894(00)00305-8

Youcai Z, Stanforth R (2001) Selective separation of lead from alkaline zinc solution by sulphide precipitation. Sep Sci Technol 36(11):2561–2570. doi:10.1081/SS-100106110

Zhang WS, Cheng CY (2007) Manganese metallurgy review. Part II: Manganese separation and recovery from solution. Hydrometallurgy 89(3–4):160–177. doi:10.1016/j.hydromet.2007.08.009

Zhao G, Wu X, Tan X, Wang X (2011) Sorption of heavy metal ions from aqueous solutions: a review. Open Colloid Sci J 4:19–31. doi:10.2174/1876530001104010019

Chapter 7
Leaching and Recovery of Molybdenum from Spent Catalysts

Mirjana Vemic, Francois Bordas, Gilles Guibaud, Piet N.L. Lens, and Eric D. van Hullebusch

Abstract Spent catalysts are generated in large quantities as solid waste on a yearly basis. Owing to their hazardous nature, environmental regulations for discarded spent catalysts are very strict. Consequently, from the ecological and economical viewpoint, metal recovery from spent catalysts is very important. Molybdenum (Mo) is one of the elements present in spent catalysts at high concentrations. The rapidly growing demands for Mo and its products create a need to develop novel recovery processes from secondary resources, i.e. spent catalysts, as there is a projected shortage of the primary resources for this element. This chapter overviews: (i) the general characteristics of Mo along with the research conducted in recent years concerning Mo chemical leaching, i.e. with strong inorganic acids, sodium hydroxide, hydrogen peroxide and acid mixtures, (ii) Mo bioleaching, i.e. with bacteria *Acidithiobacillus ferrooxidans, Acidithiobacillus thiooxidans* and *Acidianus brierleyi* or fungi *Penicillium simplicissimum* and *Aspergillus niger* and (iii) Mo recovery, i.e. precipitation, adsorption, ion exchange and solvent extraction, from spent catalysts. Chemical leaching offers Mo leaching

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M. Vemic (✉)
Université Paris-Est, Laboratoire Géomatériaux et Environnement (LGE), EA 4508, UPEM, 77454 Marne-la-Vallée, France
e-mail: mirjana.vemic@gmail.com

F. Bordas • G. Guibaud
Université de Limoges, Groupement de Recherche Eau-Sol-Environnement (GRESE), Faculté des Sciences & Techniques, 123 avenue Albert Thomas, 87060 Limoges, France
e-mail: francois.bordas@unilim.fr; gilles.guibaud@unilim.fr

P.N.L. Lens
UNESCO-IHE Institute for Water Education, Delft, The Netherlands

Department of Chemistry and Bioengineering, Tampere University of Technology, PO Box 10541, Tampere, Finland
e-mail: p.lens@un-ihe.org

E.D. van Hullebusch
Université Paris-Est, Laboratoire Géomatériaux et Environnement (LGE), EA 4508, UPEM, 77454 Marne-la-Vallée, France

UNESCO-IHE Institute for Water Education, Delft, The Netherlands
e-mail: eric.vanhullebusch@univ-mlv.fr; e.vanHullebusch@un-ihe.org

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yields exceeding 90%. Sulphuric acid seems to be the best leachant owing to its high oxidising power. Bioleaching offers more cost-efficient, simpler and more environmentally friendly processes. However, bioleaching has relatively long leaching cycles (usually around 20 days) and extraction efficiencies of Mo are below 70%. Among the recovery techniques, solvent extraction is well-established in hydrometallurgy for commercial production of high purity Mo.

Keywords Metals • Molybdenum • Secondary resources • Spent catalysts • Chemical leaching • Bioleaching • Recovery

Contents

7.1 Introduction

Molybdenum (Mo) is a valuable element to all living organisms because of its functional role in cofactors in various bacterial, plant, and animal enzymes (Giussani 2011), and its specific geochemical behaviour. Mo is extensively used in a variety of industrial processes (Fig. 7.1a) because of its high melting point, high

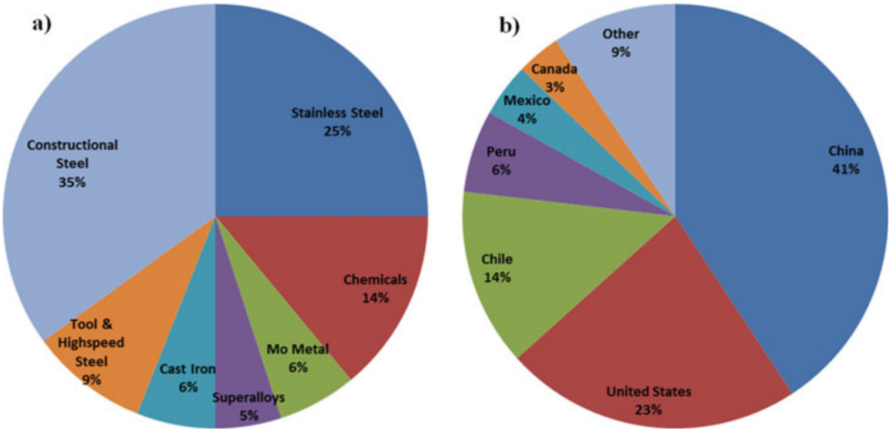

Fig. 7.1 Molybdenum application in industry (**a**) and molybdenum world production (**b**) (U.S. Geological Survey 2016)

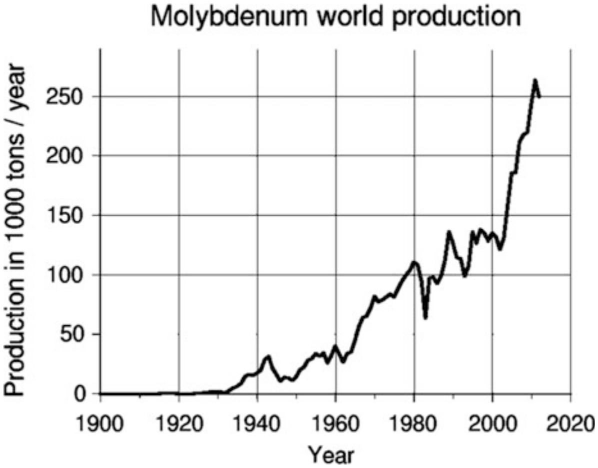

Fig. 7.2 World production of molybdenum over the years (Adapted from www.imoa.info)

strength at higher temperatures, high thermal conductivity and good corrosion resistance (Aydin et al. 2012; Das et al. 2007; Pyrzynska 2007). Therefore, Mo has widespread industrial importance (Pyrzynska 2007). Among all industrial uses, Mo catalysts are vastly utilised in petroleum desulphurisation to minimise sulphur dioxide emissions from combustion of fuel (Asghari and Mousavi 2013; Asghari et al. 2013; Cibati et al. 2013; Kar et al. 2004; Zeng and Cheng 2009a, b). Mo has also its use in alloys, corrosion inhibitors, flame-retardants and lubricants (Van Gestel et al. 2012).

The Mo world production (Fig. 7.2) increased over the years and was estimated at 266,000 tons in 2014, with the largest producers being China (100,000 t), United States (65,500 t), Chile (39,000 t), Peru (18,100 t), Mexico (11,000 t) and Canada (9500 t) (Fig. 7.1b) (U.S. Geological Survey 2016). In 2014, Mo produced at

13 mines valued 1.8 billion euros (U.S. Geological Survey 2016). Mo is an expensive element: the average market price of Mo oxide was around 13,872 € t $^{-1}$ in July of 2016 (www.infomine.com).

The high demand, high price and projected future shortage of Mo primary mineral resources creates a need to develop secondary resources and to find more beneficial ways for Mo recovery from industrial waste materials, especially spent catalysts (Marafi et al. 2007). Spent catalysts discarded by industries are undoubtedly very important, because of the inherent metals, i.e. Mo, Ni, Co, Zn, Cr, Fe, Al and W (Erust et al. 2013; Marafi et al. 2007). The worldwide generated amount of spent catalysts is in the range of 150,000–170,000 tons year^{-1} (Amiri et al. 2011; Bharadwaj and Ting 2013; Marafi and Stanislaus 2008a, b). This large quantity of spent catalysts could potentially be a suitable secondary resource of Mo.

7.2 General Characteristics of Molybdenum

7.2.1 Origin and Abundance of Molybdenum

Mo is a trace element in the Earth's crust and its estimated abundance is in the range of 0.05–40 mg kg^{-1}, with an average of 1.5 mg kg^{-1} (Aydin et al. 2012; Das et al. 2007; Kabata-Pendias and Mukherjee 2007; Zemberyova et al. 2010). The general characteristics of Mo are presented in Table 7.1. Even though Mo is found in minerals such as powellite ($CaMoO_4$), wulfenite ($PbMoO_4$) and molybdite (MoO_3) (oxidation state VI), the primary source of Mo is molybdenite (MoS_2) (oxidation state IV) (Viera et al. 2007). Mo occurs as a major component (more than 60%) in MoS_2, while the percentage of its presence in minerals such as pyrite (FeS_2), galena (PbS) and sphalerite (ZnS) is variable (Smedley et al. 2013).

Table 7.1 General characteristics of molybdenum

Name, symbol, atomic number	Molybdenum, Mo, 42
Element category	Transition metal
Mendeleev table position	Group 6
Atomic mass	95.95
Density	10.28 g cm^{-3}
Melting temperature	2623 °C
Boiling temperature	4639 °C
Thermal expansion	4.8 × 10^{-6}/K at 25 °C
Thermal conductivity	138 W/m K at 20 °C
Oxidation states	−I, −II, I, II, III, IV, V and VI
Stable isotopes	^{92}Mo, ^{93}Mo, ^{94}Mo, ^{95}Mo, ^{96}Mo, ^{97}Mo, ^{98}Mo, ^{99}Mo and ^{100}Mo

Source: Kabata-Pendias and Mukherjee (2007)

7.2.2 *Equilibria and Complexes of Molybdenum*

Figure 7.3 presents equilibria of Mo (VI) in aqueous solution (Lee et al. 2011). Table 7.2 lists the complex formation constants of Mo (VI) and formation constants for some new Mo (VI) containing species (Lee et al. 2011). Constant K is the equilibrium constant of sorption properties. When Mo concentrations exceed 10^{-3} mol L^{-1} at pH more than 6, the dominant species is the tetrahedral $MoO_4{}^{2-}$ ion (Zeng and Cheng 2009a, b). An interesting feature shown by Mo is its polymerisation (Xiong et al. 2011). Polymerisation condensation occurs when the pH is slowly decreased from 6.5 to 2.0, (Zeng and Cheng 2009a, b), giving at pH 5–6 the heptamolybdate $(Mo_7O_{24})^{6-}$ ion (Eq. 7.1), and at pH 3–5 the octamolybdate $(Mo_8O_{26})^{4-}$ ion (Eq. 7.2) (Zeng and Cheng 2009a, b):

$$7(MoO_4)^{2-}+8H^+ \rightleftharpoons (Mo_7O_{24})^{6-}+4H_2O \tag{7.1}$$

$$(Mo_7O_{24})^{6-} + (HMoO_4)^- +3H^+ \rightleftharpoons (Mo_8O_{26})^{4-}+2H_2O \tag{7.2}$$

A further pH decrease leads to anionic polymers with probably 16–18 Mo atoms (Zeng and Cheng 2009a, b).

Mo creates a vast number of complexes with different valences, i.e. hydrochloric, oxalic, thiocyanic and phosphoric molybdates (Zeng and Cheng 2009a, b). Complexes with hexavalent Mo, Mo trioxide and molybdic acid are the

Fig. 7.3 Distribution diagram of molybdenum chemical species in aqueous phase as a function of pH (Adapted from Lee et al. 2011)

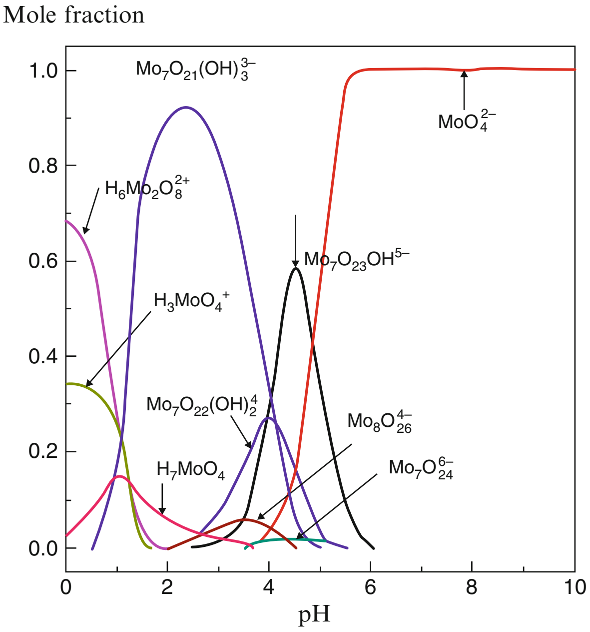

Table 7.2 Stability constants for the formation of complexes of Mo (IV) (0.01 M) in aqueous solution at 25 °C

Formula	Reaction	Log K
$H_3MoO_4^{+}$	$MoO_4^{2-} + 3H^+ \leftrightarrow H_3MoO_4^{+}$	Log $K_1 = 8.4$
MoO_2OH^+	$MoO_4^{2-} + 3H^+ \leftrightarrow MoO_2OH^+ + H_2O$	Log $K_2 = 8$
$Mo_2O_5OH^+$	$2MoO_4^{2-} + 5H^+ \leftrightarrow Mo_2O_5OH^+ + 2H_2O$	Log $K_3 = 18$
$Mo_2O_2(OH)_6^{2+}$	$2MoO_4^{2-} + 6H^+ \leftrightarrow Mo_2O_2(OH)_6^{2+}$	Log $K_4 = 19$
$Mo_7O_{24}^{6-}$	$7MoO_4^{2-} + 8H^+ \leftrightarrow Mo_7O_{24}^{6-} + 4H_2O$	Log $K_5 = 52$
$Mo_8O_{26}^{4-}$	$8MoO_4^{2-} + 12H^+ \leftrightarrow Mo_8O_{26}^{4-} + 6H_2O$	Log $K_6 = 71$
$Mo_{18}O_{56}^{4-}$	$18MoO_4^{2-} + 32H^+ \leftrightarrow Mo_{18}O_{56}^{4-} + 16H_2O$	Log $K_7 = 171$
$HMoO_4^{-}$	$MoO_4^{2-} + H^+ \leftrightarrow HMoO_4^{-}$	Log $K_8 = 3.6$
$HMo_7O_{24}^{5-}$	$7MoO_4^{2-} + 9H^+ \leftrightarrow HMo_7O_{24}^{5-} + 4H_2O$	Log $K_9 = 57$
$H_2Mo_7O_{24}^{4-}$	$7MoO_4^{2-} + 10H^+ \leftrightarrow H_2Mo_7O_{24}^{4-} + 4H_2O$	Log $K_{10} = 60$
$H_3Mo_7O_{24}^{3-}$	$7MoO_4^{2-} + 11H^+ \leftrightarrow H_3Mo_7O_{24}^{3-} + 4H_2O$	Log $K_{11} = 62$
$Mo_7O_{24}OH^{7-}$	$7MoO_4^{2-} + 7H^+ \leftrightarrow Mo_7O_{24}OH^{7-} + 3H_2O$	Log $K_{12} = 46$
$H_2Mo_6O_{21}^{4-}$	$6MoO_4^{2-} + 8H^+ \leftrightarrow H_2Mo_6O_{21}^{4-} + 3H_2O$	Log $K_{13} = 49$
$H_3Mo_8O_{28}^{5-}$	$8MoO_4^{2-} + 11H^+ \leftrightarrow H_3Mo_8O_{28}^{5-} + 4H_2O$	Log $K_{14} = 67$
$HMo_{13}O_{42}^{5-}$	$13MoO_4^{2-} + 21H^+ \leftrightarrow HMo_{13}O_{42}^{5-} + 10H_2O$	Log $K_{15} = 119$
MoO_3	$MoO_4^{2-} + 2H^+ \leftrightarrow MoO_3 + H_2O$	Log $K_{16} = 7.2$
H_2MoO_4	$MoO_4^{2-} + 2H^+ \leftrightarrow H_2MoO_4$	Log $K_{17} = 7.4$

Modified from Lee et al. (2011)

most significant ones (Zeng and Cheng 2009a, b). As a result of the activity of alkalis on MoO_3, the molybdate ion MoO_4^{2-} is formed (Zeng and Cheng 2009a, b). Mo salts such as di- and tri-molybdates can be produced by changing the quantities of MoO_3 and alkalis.

Mo (IV) is predominant in reducing conditions, while Mo (VI) in predominant in oxidising environments. Cationic species of MoO_2 are formed at pH 2.0. In stronger acid solutions (~6 N HCl), neutral MoO_2Cl_2 complexes are created (Zeng and Cheng 2009a, b). In a solution with 2–3 N HCl and H_2SO_4, anionic $MoO_2Cl_3^{-}$ and $MoO_2(SO_4)_2^{2-}$ complexes prevail (Zeng and Cheng 2009a, b).

7.3 Industrial Use of Molybdenum

7.3.1 Production of Molybdenum

The production flow sheet of Mo is presented in Fig. 7.4. Mo is obtained as a primary product from its high-grade sulphide ore, molybdenite, through oxidative roasting, purification of calcine, followed by hydrogen reduction of Mo oxide (MoO_3) (Kim et al. 2008).

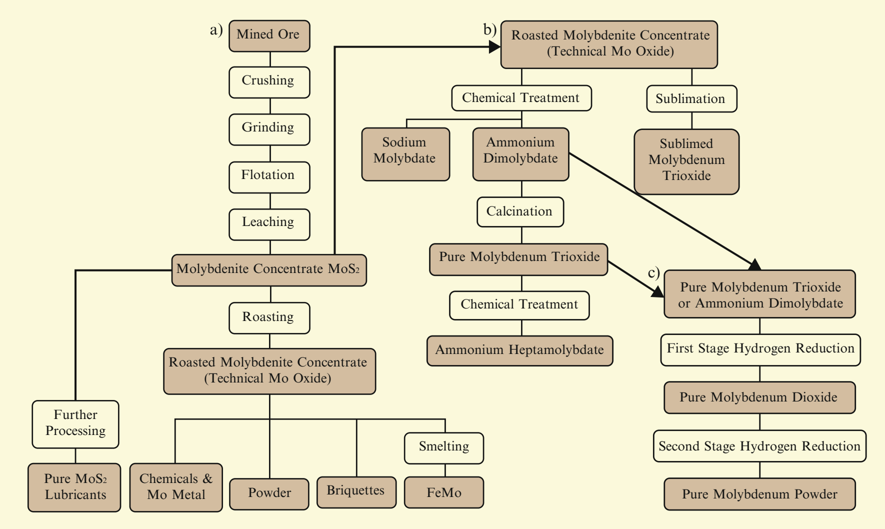

Fig. 7.4 Molybdenum production: (*a*) Crushed and ground mined ore powder after flotation step results in the 85–92% MoS_2 concentrate. Roasting in air at 500–650 °C converts MoS_2 concentrate into technical Mo oxide. (*b*) About 25% of the technical Mo oxide produced worldwide is processed into a number of chemical products. Upgrading is performed by sublimation to produce pure molybdic oxide (MoO_3) or by wet chemical processes to produce a wide range of pure Mo chemicals. (*c*) The chemical reduction of pure molybdenum trioxide or ammonium dimolybdate to metal requires two stages. The first stage, reduction to MoO_2, is performed in the 450–650 °C range. MoO_2 is then reduced to Mo metal in second stage reduction using temperatures in the 1000–1100 °C range (Modified from www.imoa.info)

7.3.2 *Molybdenum in Catalysts*

Owing to the continued world supply of crude oil and limited availability of low-sulphur crudes, catalysts are increasingly used. Catalysts not only allow for economical fuel refining, but also contribute to a safer environment through lower sulphur emissions (Akcil et al. 2015; Zeng and Cheng 2009a, b). The most common catalysts are made up of oxides of Mo and Co (or Ni) on γ-alumina support (Cibati 2011). Mo based catalysts are commonly composed of 10–30% Mo, 10–12% C, 8–12% S, 1–12% V, 1–6% Co, 0.5–6% Ni and the basis is γ-alumina (Kar et al. 2004; Marafi et al. 2007; Zeng and Cheng 2009a, b).

The Mo-based catalysts are usually prepared by soaking support solutions in which alumina is dissolved with salts of Mo, Co and Ni, after which the material is calcined at 600 °C to obtain the oxides (Marafi et al. 2010a, b). The presence of Mo oxides (MoO_3) in catalysts was verified in a study by Cedeño-Caero and Alvarez-Amparan (2014). The Ni and Co oxides exercise a promoting effect on the activity of the MoO_3-Al_2O_3 catalytic system (Cedeño-Caero and Alvarez-Amparan 2014; Cibati 2011). However, the catalyst efficiency is maximal when they are in the form of sulphides. For this reason, an initial addition of H_2S gas is required to get MoS_2

and CoS compounds that are active in catalysis. The component that catalyses the reaction is MoS_2, activated by Co, which limits the sintering of the crystals (Cibati 2011).

Because of fouling of the active catalyst surface by deposition of coke and metals, catalysts have a tendency to quickly deactivate (Akcil et al. 2015; Marafi and Stanislaus 2003). The quantity of metal-fouled spent catalysts from residue hydroprocessing units has increased significantly worldwide due to a rapid growth in the residual oil upgrading capacity by hydroprocessing (Marafi and Stanislaus 2003). Spent hydrodesulphurisation catalysts account for nearly one-third of the entire worldwide catalyst utilisation (Akcil et al. 2015; Zeng and Cheng 2009a, b), therefore they can be a considerable secondary resource of Mo.

Spent catalyst characterisation is an important part of the evaluation process when determining the ultimate fate of the catalyst and which leaching and/or recovery technique is the most suitable for metal recovery (Vemic et al. 2015). Unfortunately, very few studies have been performed concerning spent catalysts characterisation (Furimsky 1996; Mishra et al. 2007). Mo and Ni are not uniformly spread in the middle section of spent catalyst (Asghari et al. 2013). In the non-treated spent catalyst, Ni is concentrated at the surface layer, while Mo is concentrated in the lobe centre (Asghari et al. 2013). The pre-treating process triggers a migration of Mo and Ni towards the centre of the pellet (Asghari et al. 2013). Scanning electron microscopy with energy dispersive X-ray spectroscopy of the spent catalyst by Mishra et al. (2009) confirmed that the Mo matrix is firmly fixed inside a sulphur matrix, thereby having an additional diffusion barrier (Asghari et al. 2013). Vemic et al. (2015) characterized mineral sludge collected from a catalyst recycling plant where sequential extraction indicated that Mo is bound to the oxidisable and residual sludge fractions, suggesting that leaching and recovery of Mo require more energy demanding processes.

7.4 Chemical Leaching of Molybdenum from Spent Catalysts

Chemical leaching of metals is a process of extracting their minerals from a solid into the liquid phase caused by inorganic/organic leachants. This process is influenced by mineral dissolution, desorption and complexation due to the effect of pH and redox. Metal leaching is influenced by parameters such as type of leachant, particle size, presence of chelating agents, S/L ratio, temperature, contact time, stirring and pH. An optimal chelating agent displays a high leaching efficiency, a high selectivity for the target element, a high solubility and a high thermodynamic stability (De Souza Pereira et al. 2011; Goel et al. 2009; Kim et al. 2008). Since the 1970s, research on Mo leaching from industrial wastes has attracted more attention and the metal leaching with a variety of reagents such as H_2SO_4 (Kim et al. 2009a, b; Vemic et al. 2016a), HNO_3 (Khoshnevisan et al. 2012;

Sastre et al. 2002; Smirnov et al. 2010), HCl (Banda et al. 2013a), NaOH (Ghosh et al. 2015; Huang et al. 2014; Rojas-Rodríguez et al. 2012; Ruiz et al. 2011a), H_2O_2 (Park et al. 2006a, b, 2008; Ruiz et al. 2011b), NaClO (Liu et al. 2011a, b) and chemical mixtures (Barik et al. 2012a, b; De Lima et al. 2005; Lai et al. 2008; Liu et al. 2016; Park et al. 2007; Zhao et al. 2015) have been developed one after another. Table 7.3 overviews the Mo leaching technologies from spent catalysts along with the achieved leaching yields.

7.4.1 Sulphuric Acid Leaching

The possibility of Mo leaching from spent catalysts using H_2SO_4 has been evaluated by numerous studies. For instance, in one study, dissolution of metals from a pre-oxidised refinery plant spent Co-Mo/Al_2O_3 catalyst was investigated using H_2SO_4 baking (200–450 °C) followed by a leaching process (Kim et al. 2009a). Spent catalyst contained 9.92% Mo, 40% Al, 2.28% Co, 2.5% C and trace amounts of other elements such as Fe, Ni, S and P (Kim et al. 2009a). The percentage of metal dissolution has been studied under the influence of different parameters, such as time, temperature and catalyst-to-acid ratio. This study showed that the metal dissolution increased with the increase in baking temperature up to 300 °C, while it decreased with a further temperature increase (Kim et al. 2009a). More than 90% of Mo could be dissolved from the spent catalyst under optimal leaching conditions, i.e. pulp density 5% (*w*/*v*) and 2% (*v*/*v*) H_2SO_4 at 95 °C for 60 min (Kim et al. 2009a).

In another study (Kim et al. 2009b), spent catalyst that contained a different composition from the previous one, i.e. 11.6% Mo, 27.1% Al, 2.5% Ni, 9.7% S, 4.8% C, 1.9% P, 0.4% Si and trace amounts of Co and Fe, H_2SO_4 baking was investigated at 200–450 °C, also followed by a leaching process. The various baking parameters such as baking temperature, H_2SO_4 concentration and baking duration were optimised using a factorial design for maximum dissolution of Mo, Al and Ni during leaching. Under optimal baking conditions, such as 400 °C, 1:2 stoichiometric H_2SO_4 and 1 h, more than 96% of Mo was dissolved from the spent catalyst with 2% (*v*/*v*) H_2SO_4 at 80 °C (Kim et al. 2009b). Carbon and sulphur analyses of the baked samples and leaching residues indicated only 10–15% of the residual hydrocarbons had reacted during acid baking, while most of the sulphur (assumed to be metal sulphides) was converted into soluble sulphates/oxy-sulphates (Kim et al. 2009b). By comparison, in both studies, direct H_2SO_4 leaching of the catalyst resulted in low dissolution of Mo, even with excess of acid, thus revealing the valuable effect of H_2SO_4 acid baking (Kim et al. 2009a, b).

The leaching rate and yields of Mo from mineral sludge originating from a catalyst recycling plant was investigated by Vemic et al. (2016a). Different leaching reagents (stand-alone acids (nitric, sulphuric and hydrochloric) and acid mixtures (*aqua regia* (nitric + hydrochloric (1:3)), nitric + sulphuric (1:1) and nitric + sulphuric + hydrochloric (2:1:1)) were investigated at changing

Table 7.3 Overview of molybdenum leaching methods from spent catalysts and molybdenum leaching yield (%) achieved

Type of treatment	Leaching agent	Temperature (°C)	Time (h)	Other conditions	Mo leaching yield (%)	References
Sulphuric acid leaching	2% *v*/*v* H_2SO_4	95	1	Baking at 200–450 °C, pulp density 5% (*w*/*v*)	90	Kim et al. (2009a)
	2% *v*/*v* H_2SO_4	80	1	Baking at 400 °C, pulp density 5% (*w*/*v*)	96	Kim et al. (2009b)
	98% *v*/*v* H_2SO_4	80	2	Three stage successive leaching, S/L ratio 0.25 g L^{-1}		Vemic et al. (2016a)
Nitric acid leaching	3.5–4.0% *v*/*v* HNO_3	150	0.5	Pulp density 10% (*w*/*v*)	92	Khoshnevisan et al. (2012)
Hydrochloric acid leaching	10% *v*/*v* HCl	90	1	250 μm particle size, pulp density 5% (*w*/*v*)	97	Banda et al. (2013a)
Sodium hydroxide leaching	8% *v*/*v* NaOH	60	4	Roasting at 700 °C for 20 min	90	Ruiz et al. (2011a)
	5% *v*/*v* NaOH	160	2	Pulp density 4% (*w*/*v*), 300 rpm	96	Huang et al. (2014)
	20% *v*/*v* NaOH	25	2	200 rpm	95	Rojas-Rodríguez et al. (2012)

Hydrogen peroxide leaching	6% *v*/*v* H_2O_2, 40 g L^{-1} Na_2CO_3	25	1	Pulp density of 10% (*w*/*v*)	85	Park et al. (2006b)
	10% *v*/*v* H_2O_2, 85 g L^{-1} Na_2CO_3	25	1	Pulp density 20% (*w*/*v*)	84	Park et al. (2006a)
	12% *v*/*v* H_2O_2	60	1	pH 1.3, stoichiometric factor 2.4	90	Ruiz et al. (2011b)
Leaching using mixtures of chemicals	5% *v*/*v* H_2SO_4, 25% *v*/*v* HNO_3	50	5	Particle size 51–70 μm	99	Barik et al. (2012b)
	5% *v*/*v* H_2SO_4, 17% *v*/*v* H_2O_2	50	5	Particle size 51–70 μm	99	Barik et al. (2012a)
	6% *v*/*v* H_2SO_4, 30 g L^{-1} Na_2CO_3	90	1	Pulp density 10% (*w*/*v*)	98	Park et al. (2007)
	$HNO_3/H_2SO_4/HCl$ (2:1:1)	70	1	Pulp density 4% (*w*/*v*)	90	Lai et al. (2008)
Combination of chemical leaching and bioleaching	*Acidithiobacillus ferrooxidans*, 30 g L^{-1} $(NH_4)_2CO_3$	35	40	Initial ferrous ion of 2 g L^{-1}, initial pH of 2, pulp density of 10% (*w*/*v*), particle size of 106 ± 45 μm	99	Pradhan et al. (2013)

operational parameters (solid to liquid ratio, leaching time and temperature), in order to understand the leaching features and select the suitable leaching reagent which achieves the highest metal leaching yields. Sulphuric acid (98% H_2SO_4) was found to be the leachant with the highest metal leaching potential. The optimal leaching conditions were a three-stage successive leaching, temperature 80 °C, leaching time 2 h and S/L ratio 0.25 g L^{-1}. Under these conditions, 85.5% of Mo was leached out from mineral sludge.

7.4.2 Nitric Acid Leaching

HNO_3 is a successful oxidant in different leaching processes (Barik et al. 2012b; Khoshnevisan et al. 2012; Sastre et al. 2002; Smirnov et al. 2010). Additionally, the use of HNO_3 and HNO_3/H_2SO_4 mixtures as leachants results in fast metal extraction from spent catalysts (Barik et al. 2012b; Sastre et al. 2002). The effects of oxygen pressure, stirring speed, pulp density, acid concentration and temperature on the Mo leaching rate from spent catalysts were investigated by Khoshnevisan et al. (2012). The HNO_3 concentration was an important parameter in pressure leaching ($pO_2 = 965.3$ kPa) of the molybdenite concentrate (Khoshnevisan et al. 2012). At least 3.5–4% (*v*/*v*) HNO_3 was required for the leaching of a 100 g L^{-1} molybdenite concentrate, containing 92% of molybdenite (Khoshnevisan et al. 2012). Eighty-five percent of the reacted molybdenite precipitated as molybdic oxide, whereas the remaining 15% was dissolved in the liquor (Khoshnevisan et al. 2012).

7.4.3 Hydrochloric Acid Leaching

The dissolution behavior of metals in spent catalysts was investigated with respect to the HCl concentration, time and pulp density (Banda et al. 2013b). From the study, it was concluded that the particle size had a negligible effect, whereas the reaction temperature had a great effect on the metal leaching efficiency (Banda et al. 2013b). Under optimum leaching conditions, such as 10% (*v*/*v*) HCl, 90 °C, 250 μm particle size, pulp density 5% (*w*/*v*) and 60 min reaction time, it was possible to dissolve 97% of Mo (Banda et al. 2013b).

7.4.4 Sodium Hydroxide Leaching

Mo leaching from industrially roasted (800 °C for 20 min) spent $CoMo/Al_2O_3$ catalysts with NaOH was reported by Ruiz et al. (2011b). To achieve more than 85% leaching yields of Mo, the process was optimised by a factorial experimental design. Temperature, the amount of NaOH, and leaching time were the investigated parameters. Regrettably, even with the optimal leaching conditions established by the factorial design, the Mo leaching yield never exceeded 60% owing to an unfinished catalyst roasting (Ruiz et al. 2011b). Furthermore, leaching of an unroasted catalyst (comprised of 23.9% Al, 11% Mo, 7.9% S, 6.3% C and 2.9% Co) was investigated using a central composite design (CCD) (Ruiz et al. 2011b). With the changed thermal conditions (700 °C for 20 min) and by applying the optimal NaOH leaching conditions (8% (*v*/*v*) NaOH for 4 h at 60 °C), it was feasible to leach out more than 90% of Mo from the spent catalyst (Ruiz et al. 2011b).

Metal extraction from the spent Mo-Ni/Al_2O_3 catalyst was investigated by Huang et al. (2014). First, acidic oxide MoO_3 was selectively extracted by alkali leaching and then amphiprotic Al_2O_3 was dissolved by caustic soda autoclaving (Huang et al. 2014). The results showed that caustic autoclaving at low NaOH/Mo ratio could selectively extract Mo without significant dissolution of the matrix (Huang et al. 2014). Under the optimum operating conditions of temperature 160 °C, 5% (*v*/*v*) NaOH, pulp density 4% (*w*/*v*), time 120 min and stirring speed 300 rpm, over 96% of Mo was leached out (Huang et al. 2014). In another study (Rojas-Rodríguez et al. 2012), a leaching of about 95% of the Mo was achieved under the optimal leaching conditions (20% *v*/*v* NaOH, room temperature, 2 h).

7.4.5 Hydrogen Peroxide Leaching

Park et al. (2006a) investigated a hydrometallurgical processing of spent hydrodesulphurisation catalyst for Mo recovery using a H_2O_2 and Na_2CO_3 mixture. Under the optimum leaching conditions (6% (*v*/*v*) H_2O_2, 40 g L^{-1} Na_2CO_3, room temperature, 1 h) about 85% leaching of Mo was achieved (Park et al. 2006a). Similarly, the large-scale leaching of spent catalyst under optimum conditions of pulp density 20% (*w*/*v*), 10% (*v*/*v*) H_2O_2, 85 g L^{-1} Na_2CO_3 and 1 h reaction resulted in a leaching efficiency of 84% Mo (Park et al. 2006b).

Ruiz et al. (2011b) conducted a study on the feasibility of the oxidative leaching of Mo and Co sulphides contained in a spent hydrodesulphurisation catalyst using H_2O_2. The oxidative leaching of the CoMo/Al_2O_3 spent catalyst was performed with previous grinding. In a single step, at pH 1.3, pulp density 7.5% (*w*/*v*), and 12% (*v*/*v*) H_2O_2, it was possible to leach out 90% of Mo from the spent catalyst (Ruiz et al. 2011b). It was suggested that an increase in surface area and phase transformation under mechanical activation was responsible for the improved leaching recovery of Mo (Liu et al. 2011a, b).

7.4.6 Leaching Using Mixtures of Chemicals

As acid mixtures are commonly used in hydrometallurgical processes for the purpose of metal leaching, multiple studies are reported in the literature (Barik et al. 2012b). For instance, Mo and Co extraction from spent petroleum catalyst (Co-Mo/Al_2O_3) was examined utilising a H_2SO_4 and HNO_3 mixture (Barik et al. 2012b). While stand-alone H_2SO_4 was not effective as a leachant, the mixture of H_2SO_4 and HNO_3 resulted in significant recovery of both Mo and Co (Barik et al. 2012b). Under the optimal leaching conditions (5% (*v*/*v*) H_2SO_4, 25% (*v*/*v*) HNO_3, pulp density 10% (*w*/*v*), particle size 51–70 μm, temperature 50 °C and contact time 5 h), 99.7% of Mo was leached out from the spent catalyst (Barik et al. 2012b).

Barik et al. (2012a) investigated the extraction behavior of Mo, Co and Al with sulphuric acid. The spent catalyst had the following composition: 9.93% Mo, 2.24% Co, 24.09% Al and 9.12% S (Barik et al. 2012a). As in the previous study, Mo, Co and Al extraction with only H_2SO_4 was low (21.3%, 56.1% and 8.2%, respectively) because of the oxide minerals dissolution (Barik et al. 2012a). Addition of oxidants was required to dissolve elemental sulphur and sulphide minerals, hence the effect of different oxidants was investigated for possible increase in metal extraction (Barik et al. 2012a). Based on the extraction efficiency, these oxidants are ordered as follows: $H_2O_2 > HNO_3 > NaClO_3 > NaOCl$ (Barik et al. 2012a). Under optimum leaching conditions (5% (*v*/*v*) H_2SO_4, 17% (*v*/*v*) H_2O_2, pulp density 1% (*w*/*v*), particle size 51–70 μm, temperature 50 °C and time 2 h), Mo was extracted with an efficiency of 99.8% (Barik et al. 2012a).

Park et al. (2007) reported a two-stage alkali/acid leaching process to selectively target Mo and Co/Ni. During the leaching process, roasted spent catalyst (at 500 °C) was primarily treated with alkali solutions (30 g L^{-1} Na_2CO_3 at 90 °C for 1 h with pulp density 10% (*w*/*v*)) to remove Mo, and then with sulphuric acid (6% (*v*/*v*) H_2SO_4 at 90 °C for 1 h with a pulp density 10% (*w*/*v*)), resulting in a Ni and Co rich solution (Park et al. 2007; Zeng and Cheng 2009a, b). Leaching efficiencies of up to 98% for Mo were achieved (Park et al. 2007; Zeng and Cheng 2009a, b).

De Lima et al. (2005) described Mo, Ni, Co and Al leaching from spent CoMo/Al_2O_3 and NiMo/Al_2O_3 catalysts (roasted at 500 °C for 5 h) (Barik et al. 2012b). Experiments were carried out combining one, two or three chemicals, using 15 mL of each reagent (De Lima et al. 2005). The following fluoride chemicals were used: 37 wt% (~20 mol L^{-1}) HF, NaF, KF, NH_4F and NH_4HF_2 (De Lima et al. 2005). Other solubilising agents employed were HCl (12 mol L^{-1}), HNO_3 (16 mol L^{-1}), H_2SO_4 (10 mol L^{-1}) and H_2O_2 (36 wt%) (De Lima et al. 2005). Catalyst mass was fixed at 1.0 g and experiments were performed in Teflon® beakers, at 200 rpm and 50–60 °C (De Lima et al. 2005). These conditions allowed a leaching efficiency of more than 95% of Mo at 60 °C after 1 h (Barik et al. 2012b; De Lima et al. 2005).

In another study, recovering of valuable metals from spent HDS catalysts using a combined acid-leaching was investigated (Marafi et al. 2010a, b). An acid solution consisting of concentrated $HNO_3/H_2SO_4/HCl$ with a volume ratio of 2:1:1 was found to be better than the other tested solutions ($HNO_3/H_2SO_4 = 1:1$) to leach the metals out of the hydrodesulphurisation catalysts (Lai et al. 2008). For the three-acid mixture, the best pulp density and time were 4% (*w*/*v*) and 1 h, respectively at 70 °C (Lai et al. 2008). Under these conditions, the Mo leaching yields in the 1st leaching step reached 90% (Lai et al. 2008).

An oxalic acid ($H_2C_2O_4$) and hydrogen peroxide (H_2O_2) leaching-chemical precipitation process was developed to recover Mo from the spent acrylonitrile catalysts (Liu et al. 2016). Under the optimal leaching conditions ($H_2C_2O_4$ concentration of 1.25 mol L^{-1}, H_2O_2 concentration of 0.20 mol L^{-1}, leaching temperature of 50 °C, liquid-to-solid (L/S) ratio of 20 mL g^{-1} and leaching time of 2.5 h), 95% of Mo was recovered as MoO_3.

Mo was also effectively extracted from the spent diesel exhaust catalyst (V_2O_5-MoO_3/TiO_2) by using an ammonia leaching method (Zhao et al. 2015). Under the optimum conditions (the ammonia concentration of 4.5 mol L^{-1}, leaching temperature of 413.15 K, reaction time of 2 h, the H_2O_2 solution concentration of 1.0 mol L^{-1} and the liquid to solid ratio of 20/1 mL g^{-1}), the extraction efficiencies of Mo reached 95.13%.

7.4.7 Evaluation of Chemical Leaching of Molybdenum from Spent Catalysts

Hydrometallurgical approaches such as chemical leaching give Mo leaching yields of more than 90%. In spite of the good metal leaching efficiencies of chemical leaching, the leaching process itself requires continuous control, the use of high temperatures and the addition of large amounts of acid to regulate the pH and large amounts of alkali (such as NaOH) to neutralise the waste upon the end of the leaching process (Asghari et al. 2013; Zeng and Cheng 2009a, b). It is crucial that other important factors are also taken into account, e.g. costs associated with handling by-products, i.e. toxic gases (Kar et al. 2004; Marafi et al. 2010a, b). Therefore the methods which are established on utilisation of strong acids need rigorous safety precautions (Marafi et al. 2010a, b). Among all chemical leachants, sulphuric acid appears to be the optimal option since all of the target metals dissolve rapidly due to the high oxidising power of H_2SO_4 (Marafi et al. 2010a, b). Although the acid mixtures show notable advancement in the leaching efficiency in comparison with the standalone acids, the high acid utilisation and high cost present a drawback (Barik et al. 2012b; Marafi et al. 2010a, b).

7.5 Bioleaching of Molybdenum from Spent Catalysts

Bioleaching of waste has become increasingly important in recent years, owing to its vast potential, simplicity and eco-friendly operation (Chen et al. 2011; Nasernejad et al. 1999). Bioleaching utilises the potential of different microorganisms to mobilise and leach out metals from solid materials (Asghari et al. 2013; Lee and Pandey 2012). Soluble and extractable elements can be recovered owing to the ability of micro-organisms, i.e. bacteria and fungi, to modify solid compounds via the production of organic or inorganic acids (Amiri et al. 2011; Beolchini et al. 2010; Villa-Gomez et al. 2014a, b).

Two bacterial metal-leaching mechanisms have been suggested in the literature (Bayat and Sari 2010). Firstly (Eq. 7.3), bacteria interact directly with the minerals and increase the speed of mineral dissolution (biological mechanism):

$$MoS_2 + H_2O + 3.5O_2 \overset{bacteria}{\rightarrow} MoSO_4 + H_2SO_4 \tag{7.3}$$

The second mechanism involves bacterial oxidation of Fe^{2+} to Fe^{3+} (Eq. 7.4) and subsequent chemical leaching of metal-bearing minerals by Fe^{3+} (Eq. 7.5) (Bayat and Sari 2010). During this indirect (chemical) mechanism, Fe^{3+} produced by the bacteria plays a crucial role in metal solubilisation (Bayat and Sari 2010):

$$14\ Fe^{2+} + 3.5O_2 + 14\ H^+ \overset{bacteria}{\rightarrow} 14\ Fe^{3+} + 7H_2O \tag{7.4}$$

$$MoS_2 + 8H_2O + 14\ Fe^{3+} \rightarrow Mo^{4+} + 14\ Fe^{2+} + 2SO_4{}^{2-} + 16\ H^+ \tag{7.5}$$

The reaction presented in Eq. (7.4) needs the involvement of bacteria, while Eq. (7.5) is an entirely chemical process (Bayat and Sari 2010). Since Fe^{2+} created in the chemical reaction (Eq. 7.5) is reused in the iron oxidising conversion (Eq. 7.4), large quantities of heavy metals can be continuously leached out from solid substrates (Bayat and Sari 2010).

Table 7.4 overviews Mo bioleaching from spent catalysts along with its extraction efficiency. A lot of investigations (Amiri et al. 2011, 2012; Asghari and Mousavi 2013; Aung and Ting 2005; Beolchini et al. 2010, 2012; Bharadwaj and Ting 2013; Brandl et al. 2001; Chen et al. 2006b, 2011; Cibati et al. 2013; Donati et al. 1992; Gerayeli et al. 2013; Gholami et al. 2011, 2012; Lee and Pandey 2012; Mishra et al. 2008; Nasernejad et al. 1999; Pathak et al. 2009; Pradhan et al. 2010, 2013; Santhiya and Ting 2005; Shahrabi-Farahani et al. 2014; Srichandan et al. 2014; Vyas and Ting 2016) have been performed on Mo extracting from spent catalysts with mesophilic bacteria, but ended up with low Mo leaching yields (less than 70%) and relatively long leaching cycles (more than 1 day, usually 20 days). In spent catalysts Mo is strongly bound on the alumina support in the form of a MoO_3/MoS_2 (Asghari et al. 2013; Cibati 2011). As the Mo matrix is implanted inside the sulphur matrix, the attacking species needs to penetrate through the sulphur species, thus having an extra diffusion barrier (Kononova et al. 2003). Additionally, Mo is a toxic element to some bacteria (*Acidithiobacillus ferrooxidans*), and concentrations as low as 1.5–2 mg L^{-1} of Mo are enough to inhibit the micro-organism (Nasernejad et al. 1999). Therefore, the Mo speciation in the spent catalysts and its potential toxicity towards the micro-organisms explain why the bioleaching of Mo from spent catalysts is less effective than the bioleaching of other metals.

Table 7.4 Overview of molybdenum bioleaching processes from spent catalysts using different micro-organisms and molybdenum recovery (%) achieved

Type of treatment	Micro-organism used	Temp. (°C)	Time (days)	Other conditions	Mo bioleaching yield (%)	References
Bioleaching with bacteria	*A. ferrooxidans*	30	30	pH 1.8–2.0	84	Gholami et al. (2011)
	A. thiooxidans	30	30	pH 3.9–4.4	95	Gholami et al. (2011)
	A. ferrooxidans	30	5	Pulp density 5% (*w*/*v*), 20 g L^{-1} elemental sulphur	46	Mishra et al. (2008)
	A. ferrooxidans	30	21	175 rpm	40	Beolchini et al. (2010)
	A. ferrooxidans	35	1.5	Ferrous ion 2 g L^{-1}, pH 2, pulp density 10% (*w*/*v*)	53	Pradhan et al. (2013)
	A. ferrooxidans	35	7	Pulp density 0.9% (*w*/*v*), particle size 60.7 μm, aeration rate 209 mL min^{-1}	87	Shahrabi-Farahani et al. (2014)
	A. ferrooxidans + *E. coli*	30	15 + 25	Two-step bioleaching	99	Vyas and Ting (2016)
	Acidianus brierleyi	30	6	Pulp density 1% (*w*/*v*)	67	Bharadwaj and Ting (2013)
Bioleaching with fungi	*Penicillium simplicissimum*	30	5	Pulp density 4% (*w*/*v*)), sucrose (90 g L^{-1}), $NaNO_3$ (2 g L^{-1}), yeast extract (0.36 g L^{-1})	98	Amiri et al. (2011)
	Aspergillus niger	30	5	Particle size 150–212 μm, sucrose 93.8 g L^{-1}, pulp density 3% (*w*/*v*) and pH 7	99	Amiri et al. (2012)
	Aspergillus niger	30	1	pH of 5.0, rotation speed of 115 rpm, 12% inoculum	69	Gholami et al. (2012)

7.5.1 Bioleaching with Bacteria

Iron/sulphur-oxidising bacteria, such as *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans*, are commonly used micro-organisms for metal bioleaching. *A. ferrooxidans* and *A. thiooxidans* have been used for Mo, Co, Ni and Al mobilisation from the spent catalysts in batch cultures (Gholami et al. 2011). After indirect bioleaching using *A. ferrooxidans*, maximum extraction efficiencies of 84% Mo were achieved after 30 days at pH 1.8–2.0 (Gholami et al. 2011). The highest Mo extraction efficiencies using *A. thiooxidans* were 95% after 30 days at pH 3.9–4.4. The same two bacteria were used in another study for bioleaching of the exhaust catalyst rich in Mo (4.4 mg g^{-1}), Ni (4.5 mg g^{-1}) and V (9.4 mg g^{-1}) (Beolchini et al. 2010). However, the observed Mo extraction efficiencies (30–40%) were not as high as those for Ni and V (83% and 90%, respectively), as Ni and V dissolution kinetics were faster than that of Mo (Gholami et al. 2010). The achieved results have evidenced that metal solubilisation is strongly affected by the metal speciation and dissolution of the solid matrix (Beolchini et al. 2012).

Metal bioleaching from spent catalysts was attempted in a two-stage process (Mishra et al. 2008). The first stage included the change of elemental sulphur particles into sulphuric acid via oxidation by *A. ferrooxidans* (Mishra et al. 2008). In the second stage, the acidic medium (sulphuric acid) was used for the Mo, Ni and V extraction (Mishra et al. 2008). At a pulp density of 5% (*w*/*v*) of spent catalyst and 20 g L^{-1} elemental sulphur, 46.3% Mo was recovered after 7 days (Mishra et al. 2008).

Beolchini et al. (2012) conducted a bioleaching study with *A. ferrooxidans* where the experiments were performed in autoclaved 250 mL Pyrex flasks filled to a volume of 100 mL. The incubation was carried out at 30 °C and 175 rpm horizontal shaking for a maximum of 21 days using the 9 K medium ($(NH_4)_2SO_4$, 3.0 g; KCl, 0.1 g; K_2HPO_4, 0.5 g; $MgSO_4 \times 7H_2O$, 0.5 g; $Ca(NO_3)_2$, 0.01 g; deionized water, 1000 mL; and concentrated H_2SO_4, 2.5 mL (pH 2.5)) (Beolchini et al. 2012). The bioleaching yield of Mo was 40% (Beolchini et al. 2012). A bioleaching study with *A. ferrooxidans* where Mo, Ni and V were leached out from spent catalyst was reported by Pradhan et al. (2013). Under the best bioleaching conditions (initial Fe 2 g L^{-1}, initial pH 2, pulp density 10% (*w*/*v*) and temperature 35 °C), the Mo leaching efficiency was 53% (Pradhan et al. 2013).

Hydrocracking spent-catalyst bioleaching of metals (Mo, Ni, Al) was studied in a column bioreactor with *A. thiooxidans* (Shahrabi-Farahani et al. 2014). The experiments were performed in a central composite design in order to appoint the best conditions: particle size, pulp density and aeration rate (Shahrabi-Farahani et al. 2014). The best values of variables were a pulp density of 0.9% (*w*/*v*), particle size of 60.7 µm, and aeration rate of 209 mL min^{-1} to get simultaneous maximum recovery of the three metals (Shahrabi-Farahani et al. 2014). The results displayed that, under the best conditions, a maximal Mo extraction efficiency of 87% was achieved after 7 days of batch processing in the bioreactor (Shahrabi-Farahani et al. 2014).

In the literature, other types of bacteria have been used as well for bioleaching. For instance, spent hydrotreating catalyst bioleaching by the thermophilic archaea *Acidianus brierleyi* was studied (Bharadwaj and Ting 2013). The spent catalyst was characterised and the effect of pretreatment on two-step leaching was investigated at 1% *w*/*v* pulp density (Bharadwaj and Ting 2013). Pretreatment (decoking) affected the solubility of metals via oxidisation of the metal sulphides (Bharadwaj and Ting 2013). A close to 100% metal extraction efficiency was reached for Mo, Ni, Fe, and 67% for Al. Chemical (i.e. abiotic) leaching with bacterially produced H_2SO_4 resulted in lower leaching efficiencies (only up to 30%) (Bharadwaj and Ting 2013).

An enhanced extraction of Mo via a two-stage sequential process for the bioleaching of spent catalyst was described by Vyas and Ting (2016). In the first stage, two-step bioleaching was performed using *Acidithiobacillus ferrooxidans*, and achieved 20.9% Mo extraction in 15 days. To increase Mo extraction, the bioleached catalyst was subjected to a second stage bioleaching using *Escherichia coli*, during which 99% of the remaining Mo was extracted in 25 days.

7.5.2 Bioleaching with Fungi

Bioleaching with fungi is grounded on their capacity to transform solid compounds, via an indirect mechanism by the production of organic or inorganic acids, into soluble elements that can be recovered (Amiri et al. 2011). The most active leaching fungi are from the genera *Penicillium* or *Aspergillus* (Amiri et al. 2011, 2012; Gholami et al. 2012; Santhiya and Ting 2005). Amiri et al. (2011) applied statistically based experimental designs (CCD) to screen and optimise the bioleaching of spent hydrocracking catalyst by *Penicillium simplicissimum*. The combined effect of different variables (pulp density, sucrose, $NaNO_3$ and yeast extract concentrations) on metal bioleaching was investigated (Amiri et al. 2011). The optimal values of the variables for maximum metal bioleaching were pulp density (4.0% (*w*/*v*)), sucrose (90 g L^{-1}), $NaNO_3$ (2 g L^{-1}) and yeast extract (0.36 g L^{-1}) (Amiri et al. 2011). The maximal predicted Mo extraction efficiency was 97.6%. This value was consistent with the experimental values (98.8 ± 0.9% Mo) (Amiri et al. 2011).

Bioleaching experiments in batch cultures using *Aspergillus niger* in a one-step process to mobilise Mo, Co and Ni from hazardous spent catalysts were carried out by Gholami et al. (2012). Maximal Mo extraction efficiencies of 69% were achieved at a pH of 5.0, a temperature of 30 °C, a pulp density of 2 g L^{-1}, a rotation speed of 115 rpm, and using a 12% inoculum (Gholami et al. 2012).

The kinetics of bioleaching of Mo, Ni, and Al from spent hydrocracking catalyst using *Aspergillus niger* was studied by Amiri et al. (2012). The four most effective bioleaching variables were selected as follows: particle size 150–212 μm, sucrose 93.8 g L^{-1}, pulp density 3% (*w*/*v*) and pH 7 (Amiri et al. 2012). The maximum metal leaching efficiencies were 99.5% Mo (Amiri et al. 2012).

7.5.3 Combination of Chemical Leaching and Bioleaching

To leach out Mo, Ni and V present in spent refinery catalyst, two-step leaching experiments were carried out (Pradhan et al. 2013). Firstly, bioleaching was applied where Mo was leached out with a maximum recovery of 53% at optimised bioleaching conditions of an initial ferrous concentration of 2 g L^{-1}, initial pH of 2, pulp density of 10% (*w*/*v*), particle size of 106 (±45) μm and a temperature of 35 °C (Pradhan et al. 2013). Given that the quantity of leached Mo was low, a second leaching step using $(NH_4)_2CO_3$, Na_2CO_3 or H_2SO_4 was applied on the bioleached residue (Pradhan et al. 2013). With respect to Mo extraction, in the second leaching step, leaching with 30 g L^{-1} $(NH_4)_2CO_3$ obtained the best results (Pradhan et al. 2013). The percentage of extracted Mo by combining the first step and the second step with 30 g L^{-1} $(NH_4)_2CO_3$ was 99% (Pradhan et al. 2013).

7.5.4 Evaluation of Bioleaching of Molybdenum from Spent Catalysts

In comparison with chemical leaching, bioleaching can offer attractive features, especially considering environmental issues (Beolchini et al. 2010): these processes are more cost efficient (they can be performed at mild conditions), simpler (there is no need for a complex machinery) and more environmentally friendly than their chemical counterparts (Asghari et al. 2013; Zeng and Cheng 2009a, b). Some of the disadvantages are that bioleaching has relatively long leaching cycles (usually around 20 days) and extraction efficiencies of Mo are rather low (less than 70%). The bioleaching process requires only 1/5th of the cost of the chemicals needed for leaching and recovery of metals in traditional chemical methods (Pathak et al. 2009). Bioleaching processes are less costly in terms of chemical cost, but could prove costly in terms of capital cost, energy cost and maintenance cost associated with them (Pathak et al. 2009). In addition to the costs of chemicals, the costs of mixing, aeration, construction of the holding tank and operational maintenance will have to be added to the total cost when carrying out a full cost analysis (Pathak et al. 2009).

7.6 Molybdenum Recovery from Spent Catalysts

Following the solubilisation of Mo via (bio)leaching, recovery technologies to take out Mo from the leachate include (Table 7.5) precipitation (Chen et al. 2006a; Cibati et al. 2013; Mishra et al. 2007; Park et al. 2006a, b; Vemic et al. 2016b),

Table 7.5 Overview of molybdenum-recovery technologies from spent catalysts and molybdenum recovery (%) achieved

Type of treatment	Recovery agent	Temperature (°C)	Time (h)	pH	Mo recovery yield (%) achieved	References
Precipitation	Biogenic H_2S	25	5	2	36–72	Cibati et al. (2013)
	Na_2S solution	25	1.25	2	50	Vemic et al. (2016b)
	Ammonia	90	5	2	97	Park et al. (2006a, b)
	Barium hydroxide and barium aluminate	25	24	5	92	Chen et al. (2006a)
Adsorption	Activated carbon	25	3	2	99	Park et al. (2006b)
Ion exchange	Acrylic anion exchanger's AN-108P and AN-108TP	25	24	2	99	Kononova et al. (2003)
	Diphonix and AG1-x8	25	24	1.2	99	Nguyen and Lee (2013),Nguyen et al. (2013); Nguyen and Lee (2014)
Solvent extraction	Alamine® 304–1	25	4	2	99	Parhi et al. (2011)
	LIX® 973 N	25	5	1	99	Barik et al. (2014)
	LIX® 84-I and Cyanex 272	25	4	2	99	Park et al. (2010)

adsorption onto activated carbon (Afkhami and Conway 2002; Bostick et al. 2003; Derakhshi et al. 2009; Dodbiba et al. 2011; Guibal et al. 1998; Gustafsson 2003; Namasivayam and Sureshkumar 2009; Pagnanelli et al. 2011; Ryden et al. 1987), ion exchange (Henry and Van Lierde 1998; Kononova et al. 2003; Nguyen and Lee 2013; Nguyen et al. 2013; Nguyen and Lee 2014) and solvent extraction (Banda et al. 2012, 2013b; Barik et al. 2014; Guan et al. 2012; Lozano and Godinez 2003; Mishra et al. 2010; Miura et al. 2001; Parhi et al. 2011; Park et al. 2010; Sahu et al. 2013; Xia et al. 2015; Zeng and Cheng 2010; Zhang et al. 1996). Mo purification and recovery from leach liquors that simultaneously contain other extractable metals is difficult owing to co-precipitation. In this case selective recovery of metals is required, controlled manipulation of operational parameters (especially pH) needs to be applied.

7.6.1 Precipitation

7.6.1.1 Sulphide Precipitation

Precipitation is designed to precipitate metals by surpassing their solubility limits. Additional recovery can be achieved by co-precipitation or adsorption onto the precipitate during the precipitation reaction. Sulphidogenic bioreactors have been utilised to recover metals from different metal-containing waters (Cibati et al. 2013; Zeng and Cheng 2009a, 2009b). Cibati et al. (2013) assessed the feasibility of using biogenic H_2S to selectively precipitate Mo, Ni, Co and V from synthetic spent refinery catalyst leach liquor containing 15.3 g L^{-1} Mo, 4.9 g L^{-1} Ni, 2.4 g L^{-1} Co and 7.6 g L^{-1} V. The average sulphate reduction rate was 130 mg L^{-1} d^{-1} and the average dissolved sulphide concentration was 190 mg L^{-1} (Cibati et al. 2013). Biogenic H_2S allowed the selective precipitation of MoS_2 (oxidation state IV) at pH 2 with recoveries of 36–72% (Cibati et al. 2013).

Mo recovery from synthetic and real acidic leachate of a mineral sludge from a catalyst recycling plant was investigated with Na_2S solution (Vemic et al. 2016b). At first, the operational parameters (metal sulphide ratio (M/S) 0.1–1, agitation speed 0–100 rpm, contact time 15–120 min, and pH 1–5) were optimized in batch conditions on synthetic metal leachate (0.5 M HNO_3, Mo = 101.6 mg L^{-1}, Ni = 70.8 mg L^{-1}, Co = 27.1 mg L^{-1}) with a 0.1 M Na_2S solution. Additionally, recovery of the target metals was theoretically simulated with a chemical equilibrium model (Visual MINTEQ 3.0). The optimized Na_2S precipitation of metals from the synthetic metal leachate resulted in the potential selective recovery of Mo as oxide at pH 1 (98% by modelling, 95.1% experimental), after simultaneous precipitation of Ni and Co as sulphide at pH 4 (100% by modelling, 98% experimental). Metal precipitation from the real acidic leachate (18 M H_2SO_4, Mo = 10,160 mg L^{-1}, Ni = 7082 mg L^{-1}, Co = 2711 mg L^{-1}) of mineral sludge was performed with 1 M Na_2S, and resulted in a maximal Mo recovery at pH 2 (50.3%), while maximal recoveries of Ni and Co were at pH 4 (56.0 and 59.7%, respectively). Real acidic leachate gave a lower metals recovery efficiency, which can be attributed to various factors such as changes in the pH, nature of leachant, co-precipitation of Zn and competition for S^{2-} ions.

7.6.1.2 Ammonium Salt Precipitation

Precipitation of Mo from a leach solution containing 22.0 g L^{-1} Mo, 0.015 g L^{-1} Ni, 0.82 g L^{-1} Al and 8 mg L^{-1} V was investigated by Park et al. (2006a, b). An ammonium molybdate product of 97.3% purity was obtained (Park et al. 2006a, b). To convert Mo to ammonium molybdate ($(NH_4)_2MoO_4$), the solution was neutralised with ammonia at pH 11 (Zeng and Cheng 2009a, b). Subsequently, the solution was acidified by HCl to pH 2 and heated up to 90 °C to enable the formation of ammonium molybdate precipitates (Zeng and Cheng 2009a, b).

7.6.1.3 Barium Hydroxide and Barium Aluminate Precipitation

Selective precipitation of Mo from spent catalysts alkaline leachate was investigated by adding barium hydroxide and barium aluminate (Chen et al. 2006a; Zeng and Cheng 2009a, b). Mo precipitated with 92.6% efficiency at 80 °C for 40 min (Chen et al. 2006a; Zeng and Cheng 2009a, b). The precipitation of Mo is more favourable when its concentration in solution is high (above 30 g L^{-1}) (Chen et al. 2006a; Zeng and Cheng 2009a, b).

7.6.2 Adsorption

Various adsorbents, such as granular-activated carbon (Derakhshi et al. 2009; Namasivayam and Sangeetha 2006; Pagnanelli et al. 2011), pyrite (Bostick et al. 2003; Namasivayam and Sureshkumar 2009), ferrihydrite (Gustafsson 2003), high-area carbon cloth (Afkhami and Conway 2002), chitosan beans (Guibal et al. 1998), ferric oxide gel (Ryden et al. 1987) and iron-based adsorbents (Dodbiba et al. 2011) have been used for the adsorption of Mo (VI) from aqueous solution.

Activated carbon adsorption to recover Mo from spent catalyst acid leach liquors was investigated by Pagnanelli et al. (2011). Kinetic tests showed that the speed of adsorption depends on the quantity of Mo in solution (Pagnanelli et al. 2011). Equilibrium adsorption experiments showed that Mo buildup has a bell-shaped behaviour as pH changes, with a maximum adsorption capacity of around pH 5 (Pagnanelli et al. 2011). Sorption tests, performed in an activated carbon column reactor utilising leachate with a Mo concentration of 3.06 g L^{-1}, demonstrated that Mo can be removed from the leachate with an efficiency of 99% (Pagnanelli et al. 2011).

An adsorption/desorption method to recover Mo as molybdenum trioxide after leaching spent hydrodesulphurisation catalyst with sodium carbonate and hydrogen peroxide was studied by Park et al. (2006b). At the optimal adsorption conditions (pH 0.75, 3 h and pulp density 40% (*w*/*v*)), the quantity of Mo absorbed by a gram of activated carbon was 48.8 mg (Park et al. 2006b; Zeng and Cheng 2009a, b). With a pulp density of 30% (*w*/*v*) and 15% (*v*/*v*) NH_4OH at pH 9.5 for 3 h, nearly all Mo was desorbed (Zeng and Cheng 2009a, b).

7.6.3 Ion Exchange

Ion exchange is a common technology for purification, separation and decontamination of aqueous and other ion-containing solutions with solid polymeric or mineral ion exchangers (Henry and Van Lierde 1998; Kononova et al. 2003). Kononova et al. (2003) investigated the Mo adsorption abilities of the acrylic anion exchangers AN-108P and AN-108TP. The Mo recovery was conducted under static (batch experiment) and dynamic (columns) conditions (Kononova et al. 2003). In the batch experiments, the resin amounts (0.1 g, dry substance) were pre-swollen for 4 h in water with a regulated pH value and subsequently agitated in Na_2MoO_4-$NaNO_3$-H_2O (HNO_3) solutions for 24 h (Kononova et al. 2003). The quantity of resin mass to solution volume was 1:200 (Kononova et al. 2003). The Mo quantity in the resins was deliberated from the difference between initial and equilibrium concentrations of the molybdate ions in solution (Kononova et al. 2003). The Mo was desorbed by 15% aqueous ammonia solution (Kononova et al. 2003). As a result, an ammonium molybdate solution (72–155 g L^{-1} Mo) was acquired (Kononova et al. 2003). After filtration, the Mo desorption efficiency was 99.9% (Kononova et al. 2003).

Nguyen and Lee (2013), Nguyen et al. (2013), Nguyen and Lee (2014) tried separation of Mo and V from a HCl and H_2SO_4 solution containing 0.2 g L^{-1} Mo (VI) and 0.2 g L^{-1} V (V) using ion exchange. The loading behaviour of the two metals from moderate to strong acid solution was investigated using cationic (Diphonix®) and anionic (AG1-x8) resins (Nguyen and Lee 2013). The highest separation factor was obtained by ion exchange with AG1-x8 from the H_2SO_4 acid solution at pH 1.2, where no V was loaded (Nguyen and Lee 2013). The loading capacity of AG1-x8 for Mo from the H_2SO_4 solution at pH 1.2 was 176 mg g^{-1} (Nguyen and Lee 2013). Continuous column experiments demonstrated complete separation of the metals by selectively loading Mo from the feed (Nguyen and Lee 2013).

7.6.4 Solvent Extraction

A considerable effort has been made to recover Mo and V from aqueous solutions by solvent extraction using various extractants such as alamine® 336 (Lozano and Godinez 2003; Miura et al. 2001; Sahu et al. 2013), alamine® 304 (Parhi et al. 2011), alamine® 308 (Sahu et al. 2013; Zeng and Cheng 2010), trialkylamine (Banda et al. 2012), tributyl phosphate and tris (2-ethylhexyl) amine (Banda et al. 2013b), LIX® (Guan et al. 2012), Cyanex 272 (Park et al. 2007), tri-alkyl phosphine oxide and tributyl phosphate (Guan et al. 2012). A number of investigations indicated that Mo could be extracted selectively from an aqueous solution containing various other metals by chelating the extractants such as LIX® 63 (solvent extraction reagent is the water insoluble 5,8-diethyl-7-hydroxy-dodecan-6-oxime) at low and high acidities (Barik et al. 2014; Mishra et al. 2010; Park et al. 2010; Sahu et al. 2013; Zhang et al. 1996).

Parhi et al. (2011) showed that complete extraction and recovery of Mo as MoO_3 with a purity close to 100% was possible from the spent catalyst leach solution by using 10% (*v*/*v*) of Alamine® 304–1 in kerosene at pH 2.0 (Banda et al. 2012). In another study (Zeng and Cheng 2010), the separation and recovery of Mo and Co from the synthetically prepared chloride leach liquors of petroleum refining catalyst has been tested by using trioctylphosphine oxide and Alamine® 308 as extractants. The synthetically prepared leach liquor contained Mo (394 mg L^{-1}), Al (1782 mg L^{-1}) and Co (119 mg L^{-1}) in 3 M HCl (Zeng and Cheng 2010). The separation of Mo from Co and Al was achieved with 0.05 M trioctylphosphine oxide and selective recovery of Mo was attained with a combination of 0.1 M NH_4OH and 0.05 M $(NH_4)_2CO_3$ (Zeng and Cheng 2010). A Mo recovery of close to 100% was obtained from the synthetic chloride leach liquors (Kislik 2012).

Barik et al. (2014) studied leachates acquired by the acid leaching of spent HDS catalysts (containing 10.7 g L^{-1} Mo, 2.4 g L^{-1} Co and 3.8 g L^{-1} Al) for the separation and recovery of Mo (VI) utilising solvent extraction by LIX® 973 N. Extraction of Mo (VI) increased from 13.9 to 96.7% with an increase in the extractant concentration from 2.5 to 30.0% (*v*/*v*) using 30% LIX® 973 N in kerosene with a feed pH 1.0 and a phase ratio of organic to aqueous (O:A) ratio of 1:1 (Barik et al. 2014). The McCabe-Thiele plot for Mo (VI) extraction with 30% LIX® 973 N illustrated 2-stages at a 2:3 (O:A) phase ratio and the loaded extractant contained 16.0 g L^{-1} Mo (VI), demonstrating complete (99.9%) extraction (Barik et al. 2014). Stripping of Mo (VI) from the loaded organic phase was carried out with different $(NH_4)_2CO_3$ concentrations and resulted in a maximum stripping efficiency of 98.5% (Barik et al. 2014).

A baking-leaching-solvent extraction process was investigated to recover Mo from waste petroleum catalyst (Park et al. 2012). With optimal baking conditions (30 °C, 1:2 stoichiometric H_2SO_4 and baking time 1 h), and low acid leaching conditions (95 °C, 2% (*v*/*v*) H_2SO_4, pulp density 5% (*w*/*v*) and leaching time 30 min), nearly 96% Mo was dissolved (Park et al. 2012). The obtained leachate was further subjected to the solvent extraction of Mo (VI) by LIX® 84-I, followed by aluminum using Na-Cyanex 272 (Park et al. 2012). A quantitative extraction of Mo (VI) was obtained in a two-stage process with 40% LIX® 84-I and 60% Cyanex 272 (Park et al. 2012). By using 20% NH_4OH, the Mo (VI) concentration in the strip solution was enhanced up to 3 times (Park et al. 2012).

A detailed study on Mo and V separation from a spent catalyst leach solution (composed of 7.2% MoO_3, 1.7% V_2O_5, 3.7% NiO, 54.3% Al_2O_3 and 2.3% SiO_2) was performed by Sahu et al. (2013). The catalyst was roasted under oxidising atmosphere at a temperature of about 550 °C and leached in diluted sulphuric acid to solubilise Mo, V, Ni and part of the Al (Sahu et al. 2013). Metals from the leach solution were separated by solvent extraction using alamine® 304 (Sahu et al. 2013). Different parameters such as initial pH of the aqueous feed, organic to aqueous ratio (O:A) and solvent concentration were optimised until almost complete extraction and recovery were obtained for Mo (99.7%) and V (99.2%) (Sahu et al. 2013).

7.6.5 Evaluation of Molybdenum Recovery from Spent Catalysts Leach Liquors

Precipitation, adsorption, ion exchange and solvent extraction are the commonly applied technologies for Mo recovery and purification from spent catalyst leach solutions (Banda et al. 2012; Marafi and Stanislaus 2008a, b; Zeng and Cheng 2009a, b). The use of traditional recovery approaches, such as precipitation and adsorption, offers simple operations and good Mo recovery (more than 90%), but high purities of Mo are hard to achieve by these technologies (Pagnanelli et al. 2011). Ion exchange and solvent extraction offer a useful means for almost complete recovery of high purity Mo. However, these methods are very expensive and their scale of application in industry is limited (Kononova et al. 2003; Zeng and Cheng 2010). Among all these techniques, solvent extraction is mostly used in hydrometallurgy for commercial production of high purity metals (Zeng and Cheng 2009a, b).

7.7 Conclusion

In view of the ongoing depletion of the natural resources taking place worldwide, and the high price, high demand and future shortage of the primary mineral resources for Mo, it is important to implement Mo recycling/recovery/reuse from semi-finished products, by-products, secondary materials and waste, including hazardous waste, i.e. spent catalysts. Furthermore, there is a need to utilise more efficient technologies to leach and recover Mo from wastes/secondary resources in order to minimise capital outlay and environmental impact, and to respond to the increased demand for metal. This chapter summarised various methods of leaching, bioleaching and recovery of Mo from spent catalysts. The summarised results show that it is not straightforward to determine a leaching and recovery method of choice, i.e. the material requirements for the design and construction of equipment used for the Mo leaching and recovery are rather different. In addition, fluctuations in the market prices for Mo and its concentration in the spent catalysts are important factors which influence the economic viability of Mo recovery from spent catalysts.

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References

Afkhami A, Conway BE (2002) Investigation of removal of Cr(VI), Mo(VI), W(VI), V(IV) and V (V) oxy-ions from industrial waste-waters by adsorption and electrosorption at high-area carbon cloth. J Colloid Interf Sci 251:248–255. doi:10.1006/jcis.2001.8157

Akcil A, Vegliò F, Ferella F, Okudan MD, Tuncuk A (2015) A review of metal recovery from spent petroleum catalysts and ash. Waste Manag 45:420–433. doi:10.1016/j.wasman.2015.07.007

Amiri F, Mousavi SM, Yaghmaei S (2011) Enhancement of bioleaching of a spent Ni/Mo hydroprocessing catalyst by *Penicillium simplicissimum*. Separ Purif Technol 80:566–576. doi:10.1016/j.seppur.2011.06.012

Amiri F, Mousavi SM, Yaghmaei S, Barati M (2012) Bioleaching kinetics of a spent refinery catalyst using *Aspergillus niger* at optimal conditions. Biochem Eng J 67:208–217. doi:10.1016/j.bej.2012.06.011

Asghari I, Mousavi SM (2013) Effects of key parameters in recycling of metals from petroleum refinery waste catalysts in bioleaching process. Rev Environ Sci Bio Technol 13:139–161. doi:10.1007/s11157-013-9329-8

Asghari I, Mousavi SM, Amiri F, Tavassoli S (2013) Bioleaching of spent refinery catalysts: a review. J Ind Eng Chem 19:1069–1081. doi:10.1016/j.jiec.2012.12.005

Aung KMM, Ting YP (2005) Bioleaching of spent fluid catalytic cracking catalysts using *Aspergillus niger*. J Biotechnol 116:159–170. doi:10.1016/j.jbiotec.2004.10.008

Aydin I, Aydin F, Hamamci C (2012) Molybdenum speciation in asphaltite bottom ash (Seguruk, SE Anatolia, Turkey). Fuel 95:481–485. doi:10.1016/j.fuel.2011.09.013

Banda R, Sohn SH, Lee MS (2012) Process development for the separation and recovery of Mo and Co from chloride leach liquors of petroleum refining catalyst by solvent extraction. J Hazard Mater 213–214:1–6. doi:10.1016/j.jhazmat.2011.12.078

Banda R, Nguyen TH, Lee MS (2013a) Recovery of HCl from chloride leach solution of spent HDS catalyst by solvent extraction. Chem Process Eng 34:153–163. doi:10.2478/cpe-2013-0013

Banda R, Nguyen TH, Sohn SH, Lee MS (2013b) Recovery of valuable metals and regeneration of acid from the leaching solution of spent HDS catalysts by solvent extraction. Hydrometallurgy 133:161–167. doi:10.1016/j.hydromet.2013.01.006

Barik SP, Park KH, Parhi PK, Park JT (2012a) Direct leaching of molybdenum and cobalt from spent hydrodesulphurisation catalyst with sulphuric acid. Hydrometallurgy 111–112:46–51. doi:10.1016/j.hydromet.2011.10.001

Barik SP, Park KH, Parhi PK, Park JT, Nam CW (2012b) Extraction of metal values from waste spent petroleum catalyst using acidic solutions. Separ Purif Technol 101:85–90. doi:10.1016/j.seppur.2012.09.020

Barik SP, Park KH, Parhi PK, Kim DJ, Nam CW (2014) Separation and recovery of molybdenum from acidic solution using LIX 973 N. Sep Sci Technol 49:647–655. doi:10.1080/01496395.2013.862549

Bayat B, Sari B (2010) Comparative evaluation of microbial and chemical leaching processes for heavy metal removal from dewatered metal plating sludge. J Hazard Mater 174:763–769. doi:10.1016/j.jhazmat.2009.09.117

Beolchini F, Fonti V, Ferella F, Veglio F (2010) Metal recovery from spent refinery catalysts by means of biotechnological strategies. J Hazard Mater 178:529–534. doi:10.1016/j.jhazmat.2010.01.114

Beolchini F, Fonti V, Dell'Anno A, Rocchetti L, Vegliò F (2012) Assessment of biotechnological strategies for the valorisation of metal bearing wastes. Waste Manag 32:949–956. doi:10.1016/j.wasman.2011.10.014

Bharadwaj A, Ting YP (2013) Bioleaching of spent hydrotreating catalyst by acidophilic thermophile *Acidianus brierleyi*: leaching mechanism and effect of decoking. Bioresour Technol 130:673–680. doi:10.1016/j.biortech.2012.12.047

Bostick BC, Fendorf S, Helz GR (2003) Differential adsorption of molybdate and tetrathiomolybdate on pyrite (FeS_2). Environ Sci Technol 37:285–291. doi:10.1021/es0257467

Brandl H, Rehm HJ, Reed G (2001) Microbial leaching of metals. Spec Process 10:191–224. doi:10.1002/9783527620937.ch8

Cedeño-Caero L, Alvarez-Amparan MA (2014) Performance of molybdenum oxide in spent hydrodesulphurisation catalysts applied on the oxidative desulphurisation process of dibenzothiophene compounds. React Kinet Mech Cat 113:115–131. doi:10.1007/s11144-014-0729-8

Chen Y, Feng Q, Shao Y, Zhang G, Ou L, Lu Y (2006a) Investigations on the extraction of molybdenum and vanadium from ammonia leaching residue of spent catalyst. Int J Miner Process 79:42–48. doi:10.1016/j.minpro.2005.11.009

Chen Y, Feng Q, Shao Y, Zhang G, Ou L, Lu Y (2006b) Research on the recycling of valuable metals in spent Al_2O_3-based catalysts. Miner Eng 19:94–97. doi:10.1016/j.mineng.2005.06.008

Chen JW, Gao CJ, Zhang QX, Xiao LS, Zhang LQ (2011) Leaching of nickel-molybdenum sulphide ore in membrane biological reactor. Trans Nonferrous Met Soc China 21:1395–1401. doi:10.1016/S1003-6326(11)60872-8

Cibati A (2011) Development of an innovative process for the selective recovery of metals from the spent refinery catalysts. PhD thesis, University of Rome ‘La Sapienza’, Italy

Cibati A, Cheng KY, Morris C, Ginige MP, Sahinkaya E, Pagnanelli F, Kaksonen AH (2013) Selective precipitation of metals from synthetic spent refinery catalyst leach liquor with biogenic H_2S produced in a lactate-fed anaerobic baffled reactor. Hydrometallurgy 139:154–161. doi:10.1016/j.hydromet.2013.01.022

Das AK, Chakraborty R, Cervera ML, De la Guardia M (2007) A review on molybdenum determination in solid geological samples. Talanta 71:987–1000. doi:10.1016/j.talanta.2006.07.017

De Lima TS, Campos PC, Afonso JC (2005) Metal recovery from spent hydrotreatment catalysts in a fluoride-bearing medium. Hydrometallurgy 80:211–219. doi:10.1016/j.hydromet.2005.08.009

De Souza Pereira AL, Da Silva CN, Afonso JC (2011) The importance of pre-treatment of spent hydrotreating catalysts on metals recovery. Quim Nova *34*:145–150. doi:10.1590/S0100-40422011000100027

Derakhshi P, Ghafourian H, Khosravi M, Rabani M (2009) Optimisation of molybdenum adsorption from aqueous solution using granular activated carbon. World Appl Sci J 7:230–238. ISSN 1818-4952

Dodbiba G, Fujita T, Kikuchi T, Manjanna J, Matsuo S, Takahashi H, Tohji K (2011) Synthesis of iron-based adsorbents and their application in the adsorption of molybdenum ions in nitric acid solution. Chem Eng J 166:496–503. doi:10.1016/j.cej.2010.10.079

Donati E, Gurutchet G, Porro S, Tedesco P (1992) Bioleaching of metallic sulphides with *Acidithiobacillus ferrooxidans* in the absence of iron (II). World J Microbiol Biotechnol 8:305–308. doi:10.1007/BF01201885

Erust C, Akcil A, Gahan CS, Tuncuk A, Deveci H (2013) Biohydrometallurgy of secondary metal resources: a potential alternative approach for metal recovery. J Chem Technol Biotechnol 88:2115–2132. doi:10.1002/jctb.4164

Furimsky E (1996) Spent refinery catalysts: environment, safety and utilisation. Catal Today 30:223–286. doi:10.1016/0920-5861(96)00094-6

Gerayeli F, Ghojavand F, Mousavi SM, Yaghmaei S, Amiri F (2013) Screening and optimisation of effective parameters in biological extraction of heavy metals from refinery spent catalysts using a thermophilic bacterium. Sep Purif Technol 118:151–161. doi:10.1016/j.seppur.2013.06.033

Gholami RM, Borghei SM, Mousavi SM, (2010) Heavy metals recovery from spent catalyst using *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans*. In: International conference on chemistry and chemical engineering, pp 331–335. doi:10.1109/ICCCENG.2010.5560422

Gholami RM, Borghei SM, Mousavi SM (2011) Bacterial leaching of a spent Mo-Co-Ni refinery catalyst using *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans*. Hydrometallurgy 106:26–31. doi:10.1016/j.hydromet.2010.11.011

Gholami RM, Mousavi SM, Borghei SM (2012) Process optimisation and modelling of heavy metals extraction from a molybdenum rich spent catalyst by *Aspergillus niger* using response surface methodology. J Ind Eng Chem 18:218–224. doi:10.1016/j.jiec.2011.11.006

Ghosh A, Dastidar MG, Sreekrishnan TR (2015) Recent advances in bioremediation of heavy metals and metal complex dyes: review. J Environ Eng. doi:10.1061/(ASCE)EE.1943-7870.0000965

Giussani A (2011) Molybdenum in the environment and its relevance for animal and human health. Encycl Environ Health:840–846. doi:10.1016/b978-0-444-52272-6.00546-8

Goel S, Pant KK, Nigam KDP (2009) Extraction of nickel from spent catalyst using fresh and recovered EDTA. J Hazard Mater 171:253–261. doi:10.1016/j.jhazmat.2009.05.131

Guan W, Zhang G, Gao C (2012) Solvent extraction separation of molybdenum and tungsten from ammonium solution by H_2O_2-complexation. Hydrometallurgy 127–128:84–90. doi:10.1016/j.hydromet.2012.07.008

Guibal E, Milot C, Tobin JM (1998) Metal-anion sorption by chitosan beads: equilibrium and kinetic studies. Ind Eng Chem Res 37:1450–1463. doi:10.1021/ie9703954

Gustafsson JP (2003) Modeling molybdate and tungstate adsorption to ferrihydrite. Chem Geol 200:105–115. doi:10.1016/S0009-2541(03)00161-X

Henry P, Van Lierde A (1998) Selective separation of vanadium from molybdenum by electrochemical ion exchange. Hydrometallurgy 48:73–81. doi:10.1016/S0304-386X(97)00060-1

Huang S, Zhao Z, Chen X, Li F (2014) Alkali extraction of valuable metals from spent Mo-Ni/Al_2O_3 catalyst. Int J Refract Met Hard Mater 46:109–116. doi:10.1016/j.ijrmhm.2014.06.005

IMOA. International Molybdenum Association. www.imoa.info

Kabata-Pendias A, Mukherjee AB (2007) Trace elements of group VI (previously VIb). Trace elements from soil to humans. Springer, Berlin/Heidelberg/New York. Library of Congress Control Number 2007920909, 184–189

Kar BB, Datta P, Misra VN (2004) Spent catalyst: secondary source for molybdenum recovery. Hydrometallurgy 72:87–92. doi:10.1016/S0304-386X(03)00122-1

Khoshnevisan A, Yoozbashizadeh H, Mozammel M, Sadrnezhaad SK (2012) Kinetics of pressure oxidative leaching of molybdenite concentrate by nitric acid. Hydrometallurgy 111–112:52–57. doi:10.1016/j.hydromet.2011.10.002

Kim BS, Jha MK, Jeong J, Lee JC (2008) Leaching of impurities for the up-gradation of molybdenum oxide and cementation of copper by scrap iron. Int J Miner Process 88:7–12. doi:10.1016/j.minpro.2008.04.002

Kim HI, Park KH, Mishra D (2009a) Influence of sulphuric acid baking on leaching of spent Ni-Mo/Al_2O_3 hydro-processing catalyst. Hydrometallurgy 98:192–195. doi:10.1016/j.hydromet.2009.04.002

Kim HI, Park KH, Mishra D (2009b) Sulphuric acid baking and leaching of spent Co-Mo/Al_2O_3 catalyst. J Hazard Mater 166:1540–1544. doi:10.1016/j.jhazmat.2008.11.051

Kislik VS (2012) Chapter 5: Examples of application of solvent extraction techniques in chemical, radiochemical, biochemical, pharmaceutical, analytical separations, and wastewater treatment. Solv Extr: 185–314. ISBN:9780444537782

Kononova ON, Kholmogorov AG, Kachin SV, Kalyakina OP, Sadovskaya EV (2003) Ion exchange recovery of molybdenum from nitric acidic solutions using macroporous anion exchangers with long-chained cross-linking agents. Hydrometallurgy 68:83–87. doi:10.1016/S0304-386X(02)00170-6

Lai YC, Lee WJ, Huang KL, Wu CM (2008) Metal recovery from spent hydrodesulphurisation catalysts using a combined acid-leaching and electrolysis process. J Hazard Mater 154:588–594. doi:10.1016/j.jhazmat.2007.10.061

Lee JC, Pandey BD (2012) Bio-processing of solid wastes and secondary resources for metal extraction – a review. Waste Manag 32:3–18. doi:10.1016/j.wasman.2011.08.010

Lee MS, Sohn SH, Lee MH (2011) Ionic equilibria and ion exchange of molybdenum (VI) from strong acid solution. Bull Kor Chem Soc 32:3687–3691. doi:10.5012/bkcs.2011.32.10.3687

Liu W, Xu H, Yang X, Shi X (2011a) Extraction of molybdenum from lowgrade Ni-Mo ore in sodium hypochlorite solution under mechanical activation. Miner Eng 24:1580–1585. doi:10.1016/j.mineng.2011.08.010

Liu Y, Zhong H, Cao Z (2011b) Molybdenum removal from copper ore concentrates by sodium hypochlorite leaching. Min Sci Technol 21:61–64. doi:10.1016/j.mstc.2010.07.002

Liu J, Qiu Z, Yang J, Cao L, Zhang W (2016) Recovery of Mo and Ni from spent acrylonitrile catalysts using an oxidation leaching-chemical precipitation technique. Hydrometallurgy 164:64–70. doi:10.1016/j.hydromet.2016.05.003

Lozano LJ, Godinez C (2003) Comparative study of solvent extraction of vanadium from sulphate solutions by Primene 81R and Alamine 336. Miner Eng 16:291–294. doi:10.1016/S0892-6875(03)00009-8

Marafi M, Stanislaus A (2003) Studies on rejuvenation of spent residue hydroprocessing catalysts by leaching of metal foulants. J Mol Catal A Chem 202:117–125. doi:10.1007/BF00769507

Marafi M, Stanislaus A (2008a) Spent hydroprocessing catalyst waste management: a review. Part I – Developments in hydroprocessing catalyst waste reduction and use. Res Cons Rec 52:859–873. doi:10.1016/j.resconrec.2008.02.004

Marafi M, Stanislaus A (2008b) Spent hydroprocessing catalyst management: a review. Part II – Advances in metal recovery and safe disposal methods. Res Cons Rec 53:1–26. doi:10.1016/j.resconrec.2008.08.005

Marafi M, Al-Omani S, Al-Sheeha H, Al-Barood A, Stanislaus A (2007) Utilisation of metal-fouled spent residue hydroprocessing catalyst in the preparation of an active hydrodemetallisation catalyst. Ind Eng Chem Res 46:1968–1974. doi:10.1021/ie061192v

Marafi M, Stanislaus A, Furimsky E (2010a) Chapter 13: Future perspectives. Handb Spent Hydroprocess Catal:321–323. doi:10.1016/B978-0-444-53556-6.00013-6

Marafi M, Stanislaus A, Furimsky E (2010b) Chapter 11: Metal reclamation from spent hydroprocessing catalysts. Handb Spent Hydroprocess Catal:269–315. doi:10.1016/B978-0-444-53556-6.00011-2

Mishra D, Kim DJ, Ralph DE, Ahn JG, Rhee YH (2007) Bioleaching of vanadium rich spent refinery catalysts using sulphur oxidising lithotrophs. Hydrometallurgy 88:202–209. doi:10.1016/j.hydromet.2007.05.007

Mishra D, Kim DJ, Ralph DE, Ahn JG, Rhee YH (2008) Bioleaching of spent hydro-processing catalyst using acidophilic bacteria and its kinetics aspect. J Hazard Mater 152:1082–1091. doi:10.1016/j.jhazmat.2007.07.083

Mishra D, Ahn JG, Kim DJ, Chaudhury GR, Ralph DE (2009) Dissolution kinetics of spent petroleum catalyst using sulphur oxidising acidophilic micro organisms. J Hazard Mater 167:1231–1236. doi:10.1016/j.jhazmat.2009.01.056

Mishra D, Chaudhury GR, Kim DJ, Ahn JG (2010) Recovery of metal values from spent petroleum catalyst using leaching-solvent extraction technique. Hydrometallurgy 101:35–40. doi:10.1016/j.hydromet.2009.11.016

Miura K, Nozaki K, Isomura H, Hashimoto K, Toda Y (2001) Leaching and solvent extraction of vanadium ions using mixer-settlers for the recovery of the vanadium component in fly ash derived from oil burning. Solvent Extr Res Dev 2001:205–214

Namasivayam C, Sangeetha D (2006) Removal of molybdate from water by adsorption onto $ZnCl_2$ activated coir pith carbon. Bioresour Technol 97:1194–1200. doi:10.1016/j.biortech.2005.05.008

Namasivayam C, Sureshkumar MV (2009) Removal and recovery of molybdenum from aqueous solutions by adsorption onto surfactant-modified coir pith, a lignocellulosic polymer. Clean (Weinh) 37:60–66. doi:10.1002/clen.200800130

Nasernejad B, Kaghazchi T, Edrisi M, Sohrabi M (1999) Bioleaching of molybdenum from low-grade copper ore. Process Biochem 35:437–440. doi:10.1016/S0032-9592(99)00067-9

Nguyen TH, Lee MS (2013) Separation of molybdenum and vanadium from acid solutions by ion exchange. Hydrometallurgy 136:65–70. doi:10.1016/j.hydromet.2013.03.007

Nguyen TH, Lee MS (2014) Recovery of molybdenum and vanadium with high purity from sulphuric acid leach solution of spent hydrodesulphurisation catalysts by ion exchange. Hydrometallurgy 147–148:142–147. doi:10.1016/j.hydromet.2014.05.010

Nguyen TH, Sohn S, Lee MS (2013) Separation of Mo from chloride leach liquors of petroleum refining catalysts by ion exchange. Mater Trans 54:1750–1754. doi:10.2320/matertrans.M2013141

Pagnanelli F, Ferella F, Michelis ID, Veglio F (2011) Adsorption onto activated carbon for molybdenum recovery from leach liquors of exhausted hydrotreating catalysts. Hydrometallurgy 110:67–72. doi:10.1016/j.hydromet.2011.08.008

Parhi PK, Park KH, Kim HI, Park JT (2011) Recovery of molybdenum from sea nodule leach liquor by solvent extraction using Alamine 304-1. Hydrometallurgy 105:195–200. doi:10.1016/j.hydromet.2010.09.004

Park KH, Mohapatra D, Reddy BR (2006a) Selective recovery of molybdenum from spent HDS catalyst using oxidative soda ash leach/carbon adsorption method. J Hazard Mater 138:311–316. doi:10.1016/j.jhazmat.2006.05.115

Park KH, Reddy BR, Mohapatra D, Nam CW (2006b) Hydrometallurgical processing and recovery of molybdenum trioxide from spent catalyst. Int J Miner Process 80:261–265. doi:10.1016/j.minpro.2006.05.002

Park KH, Mohapatra D, Nam CW (2007) Two stage leaching of activated spent HDS catalyst and solvent extraction of aluminium using organo-phosphinic extractant, Cyanex 272. J Hazard Mater 148:287–295. doi:10.1016/j.jhazmat.2007.02.034

Park KH, Mohapatra D, Nam CW, Kim HI (2008) A noble process to recover metal values from spent hydrodesulphurisation catalyst. Geosyst Eng 11:7–12. doi:10.1080/12269328.2008.10541278

Park KH, Kim HI, Parhi PK (2010) Recovery of molybdenum from spent catalyst leach solutions by solvent extraction with LIX 84-I. Sep Purif Technol 74:294–299. doi:10.1016/j.seppur.2010.06.018

Park KH, Kim HI, Parhi PK, Mishra D, Nam CW, Park JT, Kim DJ (2012) Extraction of metals from Mo-Ni/Al_2O_3 spent catalyst using H_2SO_4 baking-leaching-solvent extraction technique. J Ind Eng Chem 18:2036–2045. doi:10.1016/j.jiec.2012.05.024

Pathak A, Dastidar MG, Sreekrishnan TR (2009) Bioleaching of heavy metals from sewage sludge: a review. J Environ Manag 90:2343–2353. doi:10.1016/j.jenvman.2008.11.005

Pradhan D, Mishra D, Kim DJ, Ahn JG, Chaudhury GR, Lee SW (2010) Bioleaching kinetics and multivariate analysis of spent petroleum catalyst dissolution using two acidophiles. J Hazard Mater 175:267–273. doi:10.1016/j.jhazmat.2009.09.159

Pradhan D, Patra AK, Kim DJ, Chung HS, Lee SW (2013) A novel sequential process of bioleaching and chemical leaching for dissolving Ni, V, and Mo from spent petroleum refinery catalyst. Hydrometallurgy 131-132:114–119. doi:10.1016/j.hydromet.2012.11.004

Pyrzynska K (2007) Determination of molybdenum in environmental samples. Anal Chim Acta 590:40–48. doi:10.1016/j.aca.2007.03.013

Rojas-Rodríguez AD, Flores-Fajardo O, Alcantar Gonzalez FS, Lopez Catillo NN, Cruz Gomez MJ (2012) Chemical treatment to recover molybdenum and vanadium from spent heavy gasoil hydrodesulphurisation catalyst. Adv Chem Eng Sci 2:408–412. doi:10.4236/aces.2012.23050

Ruiz V, Meux E, Diliberto S, Schneider M (2011a) Hydrometallurgical treatment for valuable metals recovery from spent CoMo/Al_2O_3 catalyst. 1. Improvement of soda leaching of an industrially roasted catalyst. Ind Eng Chem Res 50:5295–5306. doi:10.1021/ie102414d

Ruiz V, Meux E, Schneider M, Georgeaud V (2011b) Hydrometallurgical treatment for valuable metals recovery from spent CoMo/Al_2O_3 catalyst. 2. Oxidative leaching of an unroasted catalyst using H_2O_2. Ind Eng Chem Res 50:5307–5315. doi:10.1021/ie102428r

Ryden JC, Syers JK, Tillman RW (1987) Inorganic anion sorption and interactions with phosphate sorption by hydrous ferric oxide gel. J Soil Sci 38:211–217. doi:10.1111/j.1365-2389.1987.tb02138.x

Sahu KK, Agrawal A, Mishra D (2013) Hazardous waste to materials: recovery of molybdenum and vanadium from acidic leach liquor of spent hydroprocessing catalyst using alamine 308. J Environ Manag 125:68–73. doi:10.1016/j.jenvman.2013.03.032

Santhiya D, Ting YP (2005) Bioleaching of spent refinery processing catalyst using *Aspergillus niger* with high-yield oxalic acid. J Biotechnol 116:171–184. doi:10.1016/j.jbiotec.2004.10.011

Sastre J, Sahuquillo A, Vidal M, Rauret G (2002) Determination of Cd, Cu, Pb and Zn in environmental samples: microwave-assisted total digestion versus aqua regia and nitric acid extraction. Anal Chim Acta 462:59–72. doi:10.1016/S0003-2670(02)00307-0

Shahrabi-Farahani M, Yaghmaei S, Mousavi SM, Amiri F (2014) Bioleaching of heavy metals from a petroleum spent catalyst using *Acidithiobacillus thiooxidans* in a slurry bubble column bioreactor. *Sep Purif Technol* 132:41–49. doi:10.1016/j.seppur.2014.04.039

Smedley PL, Cooper DM, Ander EL, Milne CJ, Lapworth DJ (2013) Occurrence of molybdenum in British surface water and groundwater: distributions, controls and implications for water supply. Appl Geochem 40:144–154. doi:10.1016/j.apgeochem.2013.03.014

Smirnov KM, Raspopov NA, Shneerson YM, Lapin AY, Bitkov GA, Menshikov YA, Paskhin PN, Kirichenko VP (2010) Autoclave leaching of molybdenite concentrates with catalytic additives of nitric acid. Russ Metall 7:588–595. doi:10.1134/S0036029510070025

Srichandan H, Singh S, Pathak A, Kim DJ, Lee SW, Heyes G (2014) Bioleaching of metals from spent refinery petroleum catalyst using moderately thermophilic bacteria: effect of particle size. J Environ Sci Health 49:807–818. doi:10.1080/10934529.2014.882211

U.S. Geological Survey (2016) Mineral commodity summaries. https://minerals.usgs.gov/minerals/pubs/mcs/2017/mcs2017.pdf

Van Gestel CAM, McGrath SP, Smolders E, Ortiz MD, Borgman E, Verweij RA, Buekers J, Oorts K (2012) Effect of long-term equilibration on the toxicity of molybdenum to soil organisms. Environ Pollut 162:1–7. doi:10.1016/j.envpol.2011.10.013

Vemic M, Bordas F, Guibaud G, Joussein E, Labanowski J, Lens PNL, van Hullebusch ED (2015) Mineralogy and metals speciation in Mo rich mineral sludges generated at a metal recycling plant. Waste Manag 38:303–311. doi:10.1016/j.wasman.2014.12.021

Vemic M, Bordas F, Comte S, Guibaud G, Lens PNL, van Hullebusch ED (2016a) Acid extraction of Mo, Ni and Co from mineral sludge generated by rainfall water at a metal recycling plant. Environ Technol 37:630–639. doi:10.1080/09593330.2015.1075601

Vemic M, Bordas F, Comte S, Guibaud G, Lens PNL, van Hullebusch ED (2016b) Recovery of Mo, Ni and Co by precipitation from acidic leachate of a mineral sludge produced by a metal recycling plant. Environ Technol 10:1–12. doi:10.1080/09593330.2016.1146341

Viera M, Pogliani C, Donati E (2007) Recovery of zinc, nickel, cobalt and other metals by bioleaching. Microb Process Metal Sulf:103–119. doi:10.1007/1-4020-5589-7_5

Villa-Gomez DK, Cassidy J, Keesman KJ, Sampaio R, Lens PNL (2014a) Sulphide response analysis for sulphide control using apS electrode in sulphate reducing bioreactors. Water Res 50:48–58. doi:10.1016/j.watres.2013.10.006

Villa-Gomez DK, van Hullebusch ED, Maestro R, Farges F, Nikitenko S, Kramer H, Gonzalez-Gil G, Lens PNL (2014b) Morphology, mineralogy, and solid-liquid phase separation characteristics of Cu and Zn precipitates produced with biogenic sulphide. Environ Sci Technol 48:664–673. doi:10.1021/es402795x

Vyas S, Ting YP (2016) Sequential biological process for molybdenum extraction from hydrodesulphurisation spent catalyst. Chemosphere 160:7–12. doi:10.1016/j.chemosphere.2016.06.060

Xia Y, Xiao L, Xiao C, Zeng L (2015) Direct solvent extraction of molybdenum(VI) from sulphuric acid leach solutions using PC-88A. Hydrometallurgy 158:114–118. doi:10.1016/j.hydromet.2015.10.016

Xiong Y, Chen C, Gu X, Biswas BK, Shan W, Lou Z, Fang D, Zang S (2011) Investigation on the removal of Mo(VI) from Mo-Re containing wastewater by chemically modified persimmon residua. Bioresour Technol 102:6857–6862. doi:10.1016/j.biortech.2011.04.040

Zemberyova M, Hagarova I, Zimova J, Bartekova J, Kuss HM (2010) Determination of molybdenum in extracts of soil and sewage sludge CRMs after fractionation by means of BCR modified sequential extraction procedure. Talanta 82:582–558. doi:10.1016/j.talanta.2010.05.010

Zeng L, Cheng CY (2009a) A literature review of the recovery of molybdenum and vanadium from spent hydrodesulphurisation catalysts. Part I: Metallurgical processes. Hydrometallurgy 98:1–9. doi:10.1016/j.hydromet.2009.03.012

Zeng L, Cheng CY (2009b) A literature review of the recovery of molybdenum and vanadium from spent hydrodesulphurisation catalysts. Part II: Separation and purification. Hydrometallurgy 98:10–20. doi:10.1016/j.hydromet.2009.03.012

Zeng L, Cheng CY (2010) Recovery of molybdenum and vanadium from synthetic sulphuric acid leach solutions of spent hydrodesulphurisation catalysts using solvent extraction. Hydrometallurgy 101:141–147. doi:10.1016/j.hydromet.2009.12.008

Zhang P, Inoue K, Yoshizuka K, Tsuyama H (1996) Extraction and selective stripping of molybdenum (VI) and vanadium (IV) from sulphuric acid solution containing aluminum (III), cobalt (II), nickel (II) and iron (III) by LIX 63 in Exxsol D80. Hydrometallurgy 41:45–53. doi:10.1016/0304-386X(95)00015-9

Zhao Z, Guo M, Zhang M (2015) Extraction of molybdenum and vanadium from the spent diesel exhaust catalyst by ammonia leaching method. J Hazard Mater 286:402–409. doi:10.1016/j.jhazmat.2014.12.063

Chapter 8
Biorecovery of Metals from Electronic Waste

**Arda Işıldar, Jack van de Vossenberg, Eldon R. Rene,
Eric D. van Hullebusch, and Piet N.L. Lens**

Abstract Electronic waste, termed interchangeably as e-waste and/or waste electrical and electronic equipment (WEEE), is the fastest-growing segment of solid waste. The global electronic waste generation has reached 42 million tons in 2014, and is expected to reach 50 million tons in 2020. In addition to being a hazardous waste type, WEEE also includes relatively high concentrations of metals. Modern devices contain up to 60 different elements at various concentrations, encompassing base metals, critical metals, and platinum group metals mixed in a complex matrix of metallic and non-metallic materials. The emergence of numerous new electronic products and occurrence of complex metal mixtures make this waste stream an important secondary source of metals. Improper and informal end-of-life (EoL) processing of electronic waste has detrimental consequences on the environment and public health. Microbial processing of metals from their primary ores is an established technology with many full-scale applications. Bioprocessing of waste materials for metal recovery, on the other hand, is an emerging and promising technology with low environmental impact and high cost-effectiveness. This chapter overviews bioprocessing of electronic waste as a secondary source of metals to recover metals. Additionally, biologically-driven metal extraction technologies, (e.g. bioleaching) and metal recovery techniques (e.g. biomineralisation) are reviewed.

A. Işıldar (✉) • E.D. van Hullebusch
Université Paris-Est, Laboratoire Geomatériaux et Environnement (LGE), EA 4508, UPEM,
77454 Marne-la-Vallée, France

UNESCO-IHE Institute for Water Education, Delft, The Netherlands
e-mail: ardaisildar@gmail.com; Eric.vanHullebusch@univ-mlv.fr;
e.vanHullebusch@un-ihe.org

J. van de Vossenberg • E.R. Rene
UNESCO-IHE Institute for Water Education, Delft, The Netherlands
e-mail: j.vandevossenberg@unesco-ihe.org; e.raj@un-ihe.org

P.N.L. Lens
UNESCO-IHE Institute for Water Education, Delft, The Netherlands

Department of Chemistry and Bioengineering, Tampere University of Technology, PO Box
10541, Tampere, Finland
e-mail: p.lens@un-ihe.org

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Contents

8.1 Introduction

The amount of discarded electric and electronic devices is growing at an increasing rate and the future trends show that even larger amounts of electronic waste will be generated, in particular in growing economies (Wang et al. 2013). The global electronic waste generation reached 41.8 million tons in 2014, and is forecasted to rise to 50 million tons in 2018 (Baldé et al. 2015). Although being highly toxic, waste electrical and electronic equipment (WEEE), in particular printed circuit boards (PCB), are a promising secondary source of metals. Concentrations of copper (Cu) and precious metals, such as gold (Au), platinum (Pt) and palladium (Pd), are high as compared to natural ores (Hadi et al. 2015). It is expected that urban mining of particularly WEEE will be an important secondary source of metals in the future.

PCB are Cu-dominated materials (approx. 20–25% by weight) along with a substantial amount of precious metals. Precious metals constitute the largest fraction of value of discarded PCB and are the main economic driver of metal recovery (Cui and Zhang 2008). Currently, there is considerable research work carried out in order to develop metal-selective and environmentally friendly metal recovery technologies. There are several techniques for metal recovery, e.g. pyrometallurgy (Yang et al. 2013), hydrometallurgy (Tuncuk et al. 2012), and biohydrometallurgy (Ilyas and Lee 2015). Biomass-based processes, i.e. biohydrometallurgy, encompass a number of processes such as acidophilic (Liang et al. 2010) and cyanogenic bioleaching (Natarajan et al. 2015b), bioreduction (Yong et al. 2002), and biomineralisation (Johnston et al. 2013). They are cost-effective and environmentally friendly compared to pyrometallurgical and hydrometallurgical processes (Ilyas and Lee 2014a).

Recent developments in biotechnology, such as acclimatization of microbes to extreme bioleaching conditions, indicate that biomass-based technologies are promising alternatives to best available technologies (BAT). A comprehensive understanding of the metal mobilization mechanisms, toxicity characteristics, and process optimization enables environmental biotechnology to play a major role in metal recovery from metallurgical and electronic waste (Chapters 7 and 8 of Volume 8). Recently, very high (99%) metal removal efficiencies (Mäkinen et al. 2015) at pulp densities up to 10% (Ilyas and Lee 2014b) have been achieved with bioleaching.

Biomass-based approaches are often highlighted to play a significant role in the future of material processing for sustainable development. This not only applies to metal processing, but also to the treatment of metal containing wastes and by-products (Lee and Pandey 2012). An attractive feature of bioleaching is that it generates less pollutants compared to conventional metal processing. In this direction, an approach termed as ‘process-integrated biotechnology’ for a circular green economy has been propagated (Arundel and Sawaya 2009). The importance of biotechnology is likely to increase in the future as high grade ore deposits are being depleted. Bioleaching is expected to become increasingly an integral part of metal processing, not only for primary, but also for secondary metal sources.

8.2 Microbial Mobilisation of Metals from Electronic Waste

8.2.1 Extraction of Metals Through Biologically Mediated Reactions

Microbially mediated mobilisation of metals, termed as bioleaching, is the conversion of metals from their solid into water-soluble form and is an integral process in biohydrometallurgy. Extraction of metals from ores takes place in the presence of microorganisms that are native to these mine environments (Brierley and Brierley 2013). Biohydrometallurgy includes bioleaching and biorecovery processes, where aspects of environmental microbiology, biotechnology, hydrometallurgy, environmental engineering, mineralogy and mining engineering merge.

Naturally occurring ores are processed predominantly via conventional methods. Pyrometallurgy, i.e. thermal treatment of ores, was replaced by modern hydrometallurgy at the end of the nineteenth century when two major operations were discovered: **(1)** the cyanidation process (MacArthur-Forrest process) for precious metals and **(2)** the Bayer process for refining bauxite, the primary aluminium (Al) ore (Habashi 2005). Biohydrometallurgy, on the other hand, is considered to have begun with the identification of the acidophile *Acidithiobacillus ferrooxidans* (reclassified from *Thiobacillus ferroxidans*) as part of the microbial community found in acid mine drainage (Colmer and Hinkle 1947). The first patent for a bioleaching process was granted in 1958 to the Kennecott Mining Company, showing the involvement of *A. ferrooxidans* for Cu extraction from low-grade ore (Zimmerley et al. 1958). The patent describes a process where a leaching solution of ferric sulphate ($FeSO_4$) and sulphuric acid (H_2SO_4) is used. Ferric iron (Fe^{3+}) is regenerated by iron-oxidizing microorganisms through oxidation of ferrous iron (Fe^{2+}), and reused in a next leaching stage, making the reaction cyclic. The biochemistry of bioleaching is further explained in detail in Sects. 8.2.3.3 and 8.2.4. Following the detection of *A. ferrooxidans* in the leachates in 1961, Rio Tinto mines in the Iberian peninsula have been among the first large-scale operations in which microorganisms played a major role (Brandl 2008). Commercial applications of biohydrometallurgy were effectively initiated in 1980 at the Lo Aguirre mine in Chile (Olson et al. 2003). The mine operated between 1980 and 1996 with a capacity of about 16,000 tons/day. This was followed by the emergence of a number of full-scale plants (Brierley and Brierley 2001) and the role of bioleaching plants is increasing in the mining industry.

Today, bioleaching is increasingly used on a commercial scale for production of base metals, e.g. Cu, nickel (Ni), zinc (Zn), molybdenum (Mo), cobalt (Co), lead (Pb), and metalloids, e.g. arsenic (As), gallium (Ga), antimony (Sb) in their sulphide and oxide ores, as well as the platinum group metals, e.g. platinum (Pt), rhodium (Rh), rubidium (Ru), palladium (Pd), osmium (Os), and iridium (Ir) associated with sulphide minerals (Brierley and Brierley 2013; Watling 2015). In case of Cu, an increasing number of full-scale bioleaching plants have started to operate in the last decades (Schlesinger et al. 2011). On the other hand, recovery of metals from secondary sources using microbes is an emerging field of research. Some examples of metal-rich waste that could be regarded as a secondary source of metals are mine waste (Liu et al. 2007), slags (Yin et al. 2014b; Potysz et al. 2016), sludges (Chen and Huang 2014), contaminated soils (Deng et al. 2013), fly ashes (Ishigaki et al. 2005), spent catalyst (Lee and Pandey 2012), and electronic waste (Hong and Valix 2014).

8.2.2 Principles and Mechanisms of Microbial Leaching

8.2.2.1 Bioleaching of Metals from Waste Electrical and Electronic Equipment (WEEE)

Various biological processes, including bioleaching (microbially catalysed leaching of metals), biooxidation (oxidation of minerals by microorganisms), bioweathering (organic transformation of rocks and minerals over long time), and bioreduction (microbially induced reductive precipitation of metals) alter the chemistry and morphology of natural minerals. Acidophilic microorganisms thrive in low pH environments where microbial oxidation of minerals, e.g. pyrite (FeS), generate sulphuric acid (Rohwerder et al. 2003), resulting in the formation of acid mine drainage (Leff et al. 2015). Acidophiles are physiologically diverse, spanning across aerobic and facultative anaerobic chemolithotrophs, and various types of heterotrophic prokaryotes as well as photoautotrophic eukaryotes (Xie et al. 2007). Mesophilic, thermophilic and hyperthermophilic species are commonly found in bioleaching environments (Rawlings and Johnson 2007).

Acidophilic microorganisms keep their intracellular pH close to neutrality and maintain a proton gradient over their cytoplasmic membranes (van de Vossenberg et al. 1998). Extracellular enzymes of acidophiles are optimally active at low pH (Bonnefoy and Holmes 2012). Iron- and sulphur-oxidizer acidophiles are found in low pH environments and gain energy by oxidation of $Fe^{2+}$and inorganic sulphur compounds (Sand et al. 2001). They are also found in natural waters, sewer pipes causing corrosion problems, caves forming snottites (a layer of biomass which hang from the walls and ceilings of caves), hydrothermal vents and geysers (Rawlings and Johnson 2007).

Biomining has progressed from rather uncontrolled dump leaching to processing of refractory ores in designed bio-heaps (Olson et al. 2003). Stirred tank bioprocessing has also been developed and commercialised to full scale (Acevedo 2000). In bioleaching of sulphide minerals, the microorganisms play a catalytic role to oxidize Fe^{2+} to ferric (Fe^{3+}) iron and elemental sulphur (S^0) to sulphate $\left(SO_4^{2-}\right)$ generating acid (Watling 2006). Dissolution of certain metal sulphides yields thiosulphate as an intermediate, which is further oxidised to sulphuric acid (H_2SO_4) (Vera et al. 2013). Most of these microorganisms use atmospheric carbon dioxide as their carbon source and grow chemolithoautotrophically (Kimura et al. 2011).

In addition to acidophilic chemolithotrophic microorganisms, heterotrophic neutrophilic cyanide-generating microbes can be used in bioleaching (Kaksonen et al. 2014). Many ubiquitous microorganisms are known to generate cyanide under certain conditions. Cyanide is the general name for the compounds consisting of a carbon atom triple-bonded to a nitrogen atom. They have a high affinity to bond transition metals. Some soil bacteria, e.g. strains of *Chromobacterium violaceum* (Faramarzi et al. 2004), *Pseudomonas fluorescens* (Campbell et al. 2001), *Pseudomonas aeruginosa* (Fairbrother et al. 2009), as well as several fungal species, e.g. *Pleurotus ostreatus* (Brandl and Faramarzi 2006) and algae, e.g. *Chlorella* *vulgaris* (Mata et al. 2009), have the ability to metabolize cyanide. They can be used in the processing of waste materials for base and precious metal extraction.

8.2.2.2 Dissolution of Metal Sulphides via the Thiosulphate and Polysulphide Mechanisms

In this section, dissolution mechanisms of metals from their primary ores (metal sulphides) are reviewed. Despite similarities with metal sulphides, the main mechanism of metal bioleaching from anthropogenic waste material have still not been well understood. The main peculiarity of secondary resources, such as waste material, is the speciation of metals (Tuncuk et al. 2012). The metals are found in their elemental form or in various alloys. Due to the difference in chemical composition, the dissolution mechanisms of elemental metals in the waste material also show differences.

Dissolution of metal sulphides can follow two different pathways: the thiosulphate and the polysulphide pathway (Rohwerder et al. 2003). In general, dissolution is achieved by a combination of acidic leaching (proton attack) and oxidation processes. The reaction pathway is determined by the mineral species (Vera et al. 2013). The reactivity of metal sulphides with the protons is a significant criterion. Acid-insoluble sulphides, such as pyrite (FeS_2) are attacked through the thiosulphate mechanism, which depends on the oxidative attack of ferric ions in solution. Acid soluble sulphides, such as chalcopyrite ($CuFeS_2$), are degraded through the polysulphide mechanism, as shown in Fig. 8.1.

Fe^{3+} ions extract electrons from the mineral and are thereby reduced to the Fe^{2+} form. Consequently, the mineral releases metal cations and intermediate sulphur compounds. Iron-oxidizing bacteria catalyse the Fe^{3+}/Fe^{2+} cycle. In the case of the thiosulphate mechanism (acid-insoluble metal-sulphide mineral), an additional attack is performed by protons. The sulphur compounds are oxidized by sulphur-oxidizing bacteria and abiotically. Figure 8.1 shows the main reaction products that highlighted in boxes, e.g. elemental sulphur in thiosulphate and sulphuric acid in polysulphide mechanism. The main reaction products accumulate in the absence of sulphur-oxidizing microorganisms.

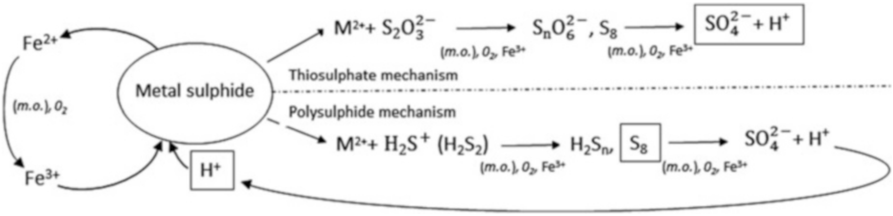

Fig. 8.1 Polysulphide and thiosulphate leaching mechanisms of metal sulphide minerals by acidophile microorganisms (m.o.), redrawn from Donati and Sand (2007))

8.2.2.3 Physical Contact Mechanism: Contact, Non-contact, and Cooperative Leaching

Microbe-mineral interactions in bioleaching are explained by direct and indirect mechanisms (Watling 2006). Metals are dissolved from minerals either directly by the metabolism of the cell or indirectly by the metabolic products. Direct mechanisms require close contact to the mineral, where microorganisms obtain electrons directly from the mineral, also termed as contact mechanism. In the indirect or non-contact mechanism, the microorganisms are not attached to the surface, but instead they catalyse the oxidation of minerals by producing a leaching agent. In practice, a combination of both the contact and non-contact mechanism is involved, where the attached bacteria and the oxidizing agent in the solution play a role, termed cooperative leaching (Rohwerder et al. 2003). The oxidation of the matrix is based on the activity of acidophilic chemolithotrophic iron-and sulphur-oxidizing microorganisms.

Figure 8.2 shows the contact, non-contact and collaborative leaching mechanism of metals from primary minerals. In the contact mechanism, a close contact is required where cells are attached to the mineral surface. It was shown using radioactively labelled carbon (^{14}C) that a significant fraction of *A. ferrooxidans* cells grow attached to the mineral on $NaHCO_3$ (Escobar et al. 1996). The chemotactic behaviour of *Leptospirillum ferrooxidans* to metal ions has been demonstrated (Acuna et al. 1992). Moreover, genes involved in chemotaxis were detected in *A. ferrooxidans* and *A. thiooxidans* (Valdés et al. 2008b). Contact bioleaching of the mineral occurs even in the absence of ferric ions. This explains the bioleaching of iron-free sulphides through the contact mechanism (Rohwerder et al. 2003).

When minerals are bioleached, microorganisms metabolise lixiviants, either through direct electron transfer or indirectly, and create the space in which bioleaching takes place. The extracellular polymeric substances (EPS) may serve as the reaction space and many complex bioleaching reactions take place within this EPS layer, rather than in the solution (Sand et al. 2001). The space between the cell wall and the surface is considered as the reaction space. Many species typically form biofilms from an EPS layer when they attach to the surface of a mineral (Ghauri et al. 2007). Bioleaching of metals from WEEE shows a similar pattern, as explained later in Sect. 8.2.4.

8.2.3 Metal-Mobilization Mechanisms

A number of metal mobilization mechanisms are defined, namely **(i)** acidolysis (formation of acids), **(ii)** complexolysis (excretion of complexing agents), and **(iii)** redoxolysis (microbially induced or catalysed oxidation and reduction reactions) for the biologically induced dissolution of metals from primary ores (Bosecker

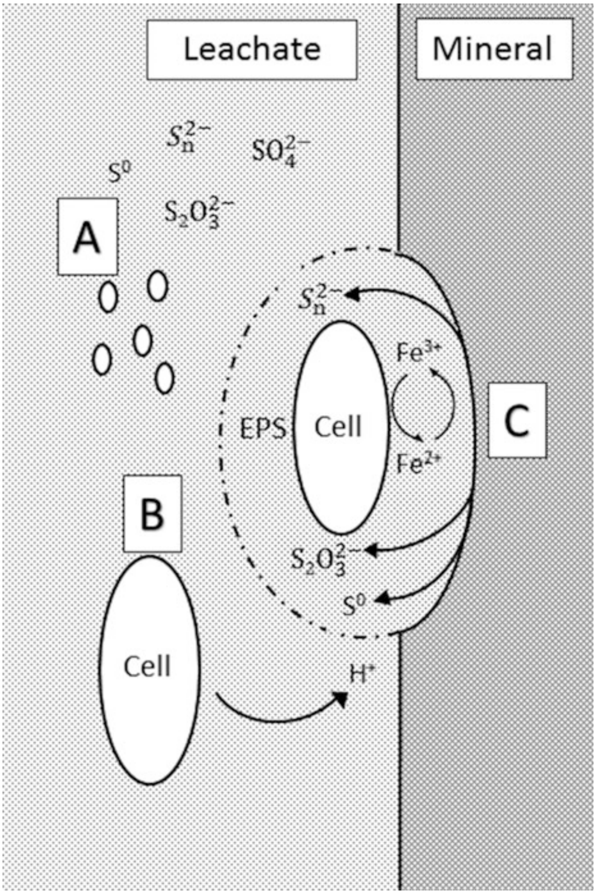

Fig. 8.2 Schematic mechanisms of cooperative bioleaching: Sulphur oxidation (*A*), non-contact (*B*), and contact (*C*) mechanisms (Redrawn from Tributsch 2001 and Brandl 2008)

1997; Brandl 2008). Bioprocessing of secondary raw materials typically include a combination of these metal dissolution mechanisms.

8.2.3.1 Acidolysis

In the acidolysis mechanism, the dissolution of metals occurs by metabolic acids (Vera et al. 2013). A list of microorganisms that can perform acidolysis is given in Table 8.1. Microorganisms catalyse the protonic mechanism, in which they excrete protons that weaken the metal ion bond, thus bringing the metal into solution. In most cases, mineral solubilization occurs simultaneously in the presence of the metabolic ligands under acidic conditions (Brandl and Faramarzi 2006). In bioleaching of metals from waste materials, the prerequisite is that the bonds between metal ions and ligands are stronger than those between metal ions and solid particles. In that case, the metal is successfully leached from the solid particles

Table 8.1 Microorganisms involved in bioleaching

Microorganism	Leaching mechanism	Temperature optimum	pH optimum	References
Archaea				
Acidianus brierleyi	Acidolysis (H_2SO_4), redoxolysis (Fe^{3+})	Thermophilic (70 °C)	1.5–2	Brierley and Brierley (1986) and Nemati and Harrison (2000)
Ferroplasma acidarmanus	Acidolysis (H_2SO_4), redoxolysis (Fe^{3+})	Moderately thermophilic (42 °C)	0.5–1.2	Edwards et al. (2000)
Ferroplasma cupricumulans	Redoxolysis (Fe^{3+})	Moderate thermophilic (54–63 °C)	1.0–1.2	Hawkes et al. (2006)
Ferroplasma acidiphilum	Redoxolysis (Fe^{3+})	Mesophilic (15–45 °C)	1.3–2.2	Golyshina et al. (2000)
Metallosphaera hakonensis	Acidolysis (H_2SO_4)	Thermophilic (55–80 °C)	1.0–4.0	Plumb et al. (2008)
Metallosphaera prunae	Acidolysis (H_2SO_4)	Thermophilic (55–80 °C)	1.0–4.5	Fuchs et al. (1995)
Metallosphaera sedula	Acidolysis (H_2SO_4)	Thermophilic (75 °C)	1.0–4.5	Huber et al. (1989)
Metallosphaera sedula	Acidolysis (H_2SO_4), redoxolysis (Fe^{3+})	Thermophilic (75 °C)	1.0–4.5	Auernik et al. (2008)
Metallosphaera yellowstonensis	Acidolysis (H_2SO_4), redoxolysis (Fe^{3+})	Thermophilic (65 °C)	2.5–3.5	Kozubal et al. (2011)
Sulfolobus acidocaldarius	Acidolysis (H_2SO_4), redoxolysis (Fe^{3+})	Extreme thermophilic (55–85 °C)	2.0–3.0	Plumb et al. (2002)
Sulfolobus solfataricus	Acidolysis (H_2SO_4), redoxolysis (Fe^{3+})	Extreme thermophilic (55–87 °C)	2.0–3.0	Plumb et al. (2002)
Sulfolobus metallicus	Acidolysis (H_2SO_4), redoxolysis (Fe^{3+})	Thermophilic (50–75 °C)	2.0–3.0	Brandl et al. (2008) and Kaksonen et al. (2014)
Sulfolobus yangmingensis	Acidolysis (H_2SO_4)	Extreme thermophilic (80 °C)	4.0	Jan et al. (1999)
Thermoplasma acidophilum	Acidolysis (H_2SO_4), redoxolysis (Fe^{3+})	Moderately thermophilic (55–60 °C)	1.0–2.0	Darland et al. (1970) and Ilyas et al. (2010)
Bacteria				
Acidimicrobium ferrooxidans	Redoxolysis (Fe^{3+})	Moderately thermophilic (45–50 °C)	2.0	Clark and Norris (1996)
Acidithiobacillus caldus	Acidolysis (H_2SO_4)	Moderately thermophilic (42–45 °C)	2.0–2.5	Zhou et al. (2007)

(continued)

Table 8.1 (continued)

Microorganism	Leaching mechanism	Temperature optimum	pH optimum	References
Acidithiobacillus ferrooxidans	Acidolysis (H_2SO_4), redoxolysis (Fe^{3+})	Mesophilic (28–35 °C)	2.5	Silverman and Lundgren (1959) and Kelly and Wood (2000)
Acidithiobacillus thiooxidans	Acidolysis (H_2SO_4)	Mesophilic (28–30 °C)	1.0–3.0	Joffe (1922) and Bosecker (1997)
Ferrimicrobium acidiphilum	Redoxolysis (Fe^{3+})	Mesophilic (35 °C)	1.4–2.0	Johnson et al. (2009)
Ferrithrix thermotolerans	Redoxolysis (Fe^{3+})	Moderately thermophilic (43–50 °C)	1.6–1.8	Johnson et al. (2009)
Ferrovum myxofaciens	Redoxolysis (Fe^{3+})	Mesophilic (20–30 °C)	1.0–2.0	Fabisch et al. (2013)
Leptospirillum ferriphilum	Redoxolysis (Fe^{3+})	Moderately thermophilic (42 °C)	1.2–1.6	Spolaore et al. (2011)
Leptospirillum ferrooxidans	Redoxolysis (Fe^{3+})	Mesophilic (28–35 °C)	1.8	Sand et al. (1992)
Leptothrix discophora	Redoxolysis (Fe^{3+})	Mesophilic (15–40 °C)	5.8–7.8	Corstjens et al. (1992)
Chromobacterium violaceum	Complexolysis (CN^-)	Mesophilic (25–37 °C)	7.0–7.5	Campbell et al. (2001)
Pseudomonas aeruginosa	Complexolysis (CN^-)	Mesophilic (25–35 °C)	7.0–7.8	Castric (1977)
Pseudomonas fluorescens	Complexolysis (CN^-)	Mesophilic (25–35 °C)	7.0–7.8	Blumer and Haas (2000)
Pseudomonas putida	Acidolysis (citrate), complexolysis (CN^-)	Mesophilic (25–35 °C)	7.0–8.2	Brandl and Faramarzi (2006)
Sulfobacillus sibiricus	Acidolysis (H_2SO_4), redoxolysis (Fe^{3+})	Moderately thermophilic (45–55 °C)	1.7–2.0	Melamud et al. (2003)
Sulfobacillus thermosulfioxidans	Acidolysis (H_2SO_4), redoxolysis (Fe^{3+})	Moderately thermophilic (40–60 °C) (50 °C)	1.7–2.0	Golovacheva and Karavaiko (1978)
Fungi				
Aspergillus awamori	Acidolysis (citrate), complexolysis (oxalate)	Mesophilic (28 °C)	6.8–7.2	Mapelli et al. (2012)
Aspergillus flavus	Acidolysis (organic acids)	Mesophilic (30 °C)	6.5	Mishra et al. (2009)
Aspergillus fumigatus	Acidolysis (citrate), complexolysis (oxalate)	Mesophilic (30 °C)	6.6–7.2	Brandl (2008)

(continued)

Table 8.1 (continued)

Microorganism	Leaching mechanism	Temperature optimum	pH optimum	References
Aspergillus niger	Acidolysis (citrate, oxalate), complexolysis (CN^-)	Mesophilic (30 °C)	6.4–7.3	Xu and Ting (2009))
Cladosporium oxysporum	Acidolysis (organic acids)	Mesophilic (30 °C)	6.5	Mishra et al. (2009))
Penicillium chrysogenum	Acidolysis (organic acids)	Mesophilic (30 °C)	6.7	Deng et al. (2013)
Penicillium simplicissimum	Acidolysis (citrate, oxalate)	Mesophilic (30 °C)	6.0–7.0	Brandl et al. (2001)

into the solution. Acidolysis is performed by several autotrophic sulphur oxidizers and heterotrophic fungal and bacterial cells.

8.2.3.2 Complexolysis

In the complexolysis mechanism, metal solubilisation is induced by a metabolic ligand which increases the metal mobility by complexation and/or chelation. Biogenic complexing agents bind with metals, replacing bonds, leading to solubilisation of the metals. Siderophores, secreted by a number of bacteria and fungi, are amongst the strongest soluble iron (Fe^{3+}) binding agents known (Rawlings 2005). Fe^{3+} is found mostly insoluble in natural waters. Apart from Fe^{3+}, siderophores can also bind and solubilise other metals (Neilands 1995; Del Olmo et al. 2003).

The complexolysis mechanism is largely performed by heterotrophic cyanide-generating microorganisms. Cyanide is the general term for chemicals which contain a cyano group with the chemical formula CN^-. Humans have trace amounts of thiocyanide (SCN^-) in saliva, urine, and gastric juices (Zammit et al. 2012). Cyanide reacts with metals in the waste material as a complexing agent and forms soluble metal-cyanide complexes (Rees and van Deventer 1999). In particular, recovery of noble metals from secondary sources is focused on the utilisation of cyanogenic bacteria. Precious metals such as Au, Pt, and Pd are among the most chemically stable elements, and react only with a limited number of chemicals. Safety issues regarding cyanide can be minimised because cyanogenic bacteria autonomously decompose cyanide to nontoxic β-*cyanoalanine* (Knowles 1976). Thus, the biological cyanide production process enables the design of a system without the need of an additional CN^- treatment or detoxification of this compound (Shin et al. 2013). Cyanide-complexed metals can be subsequently recovered using various methods, such as activated carbon adsorption, cementation, electrowinning or electrorefining.

8.2.3.3 Redoxolysis

In the redoxolysis mechanism, microorganisms produce catalytic compounds which regulate the oxidation potential of the solution. The leaching efficiency and rate depend on the mineral phase, type of metal and oxidation state (Mishra and Rhee 2014). Ferric iron (Fe^{3+}) is one of the most common redoxolysis agents in leaching systems. It is produced by iron oxidizers and is reduced to ferrous iron (Fe^{2+}) in the bioleaching reaction, but then re-oxidized by iron-oxidisers to Fe^{3+}, making the reaction cyclic (Schippers et al. 1996).

The thermodynamic equilibrium of reactions with Cu, Zn, and Ni can be elucidated on the basis of enthalpy and Gibbs free energy values under normal conditions, given below in Eqs. (8.1), (8.2), and (8.3).

$$Cu^0 + 2Fe^{3+} \rightarrow Cu^{2+} + 2Fe^{2+} \left(\Delta G^0 = -347.1\,\mathrm{kJ}\right) \tag{8.1}$$

$$Ni^0 + 2Fe^{3+} \rightarrow Ni^{2+} + 2Fe^{2+} \left(\Delta G^0 = -822.6\,\mathrm{kJ}\right) \tag{8.2}$$

$$Zn^0 + 2Fe^{3+} \rightarrow Zn^{2+} + 2Fe^{2+} \left(\Delta G^0 = -1235.9\,\mathrm{kJ}\right) \tag{8.3}$$

Fe^{3+} acts as an oxidising agent, and readily oxidises metals, leading to their dissolution. Also, many microbial strains have the ability to reduce Fe^{3+} to Fe^{2+} under anaerobic conditions (Rawlings 2005). The reaction has a standard reduction potential of 0.77 V relative to a standard hydrogen electrode (SHE). The redox potential is an essential parameter highly useful to estimate and understand the chemistry and speciation of iron (Yue et al. 2016). In bioleaching environments, an increased redox potential is observed owing to the activity of iron-oxidizing microorganisms. The redox chain from Fe^{2+} ions to the final electron acceptor oxygen has been shown for mesophilic acidophilic iron oxidizers (Brasseur et al. 2004).

8.2.4 Bioleaching of Metals from Electronic Waste Materials

Reported Cu bioleaching efficiencies vary widely from 50 to 100% with leaching periods typically exceeding 5 days and pulp densities of 1–3% (*w*/*v*). Several studies have demonstrated improved bioleaching efficiencies in sulphur and ferrous iron-supplemented media (Wang et al. 2009; Ilyas et al. 2010; Liang et al. 2010). A summary of the recent literature is given in Table 8.2.

From a recycling point of view, the main peculiarity of the electronic waste material is that the metals are present in their zero-valent elemental state (Tuncuk et al. 2012). Metal mobilization from waste materials by acidophiles involves an indirect leaching mechanism by biogenic reagents such as sulphuric acid (H_2SO_4) and ferric iron (Fe^{3+}) produced in the first stage. In addition, the importance of bacterial attachment to electronic waste material has been recently demonstrated:

Table 8.2 Bioleaching of metals from printed circuit boards via various mechanisms

Microorganism(s)	Leaching mechanism	T°C	pH	Reactor type	Pulp density (*w*/*v*)	Leached metals (percentage, mg/g printed circuit boards)	References
Acidithiobacillus thiooxidans	Acidolysis (H_2SO_4)	30 °C	0.5	Batch reactor	1%	**Cu** 98% (832 mg/g)	Hong and Valix (2014)
Aspergillus niger, *Penicillium simplicissimum*	Acidolysis (organic acids)	30 °C	3.5	Batch reactor	1%	**Cu** 65% (52 mg/g), **Al** 95% (225 mg/g), **Ni** 95% (14 mg/g), **Zn** 95% (25 mg/g)	Brandl et al. (2001)
Chromobacterium violaceum (metabolically engineered)	Complexolysis (CN^-)	30 °C	Neutral	Batch reactor	0.5%	**Au** 31% (0.04 mg/g)	Tay et al. (2013)
Sulfobacillus thermosulfidooxidans, acidophilic isolate	Acidolysis (H_2SO_4), Redoxolysis (Fe^{3+})	45 °C	1.2–2.0	Batch reactor	1%	**Cu** 89% (76 mg/g), **Ni** 81% (16.2 mg/g), **Zn** 83% (66.4 mg/g)	Ilyas et al. (2007)
Acidithiobacillus sp., *Gallionella* sp., *Leptospirillum* sp.	Redoxolysis (Fe^{3+})	30 °C	1.5–2.5	Batch reactor	2%	**Cu** 95% (219 mg/g)	Xiang et al. (2010)
Chromobacterium violaceum, *Pseudomonas fluorescens*, *Pseudomonas plecoglossicida*	Complexolysis (CN^-)	30 °C	7.2–9.2	Batch reactor	various	**Au** 69% (not specified)	Brandl et al. (2008)
Acidophilic consortium (genera Acidithiobacillus and Gallionella)	Redoxolysis (Fe^{3+})	30 °C	2.0	Batch reactor	1.2%	**Cu** 97% (626 mg/g), **Al** 88% (34 mg/g), **Zn** 92% (28 mg/g)	Zhu et al. (2011)
A. ferrooxidans, *A. thiooxidans*	Redoxolysis (Fe^{3+})	28 °C	1.8–2.5	Batch reactor	0.8–1.9%	**Cu** 99% (90 mg/g)	Wang et al. (2009)
A. ferrooxidans, *Leptospirillum ferrooxidans*, *A. thiooxidans*	Acidolysis (H_2SO_4), redoxolysis (Fe^{3+})	25 °C	1.7	Batch reactor	1%	**Cu** 95% (106 mg/g)	Bas et al. (2013)
A. ferrooxidans, *A. thiooxidans*	Acidolysis (H_2SO_4), redoxolysis (Fe^{3+})	28 °C	1.5–3.5	Batch reactor	3% (increased gradually)	**Cu** (94%), **Ni** (89%), **Zn** (90%)	Liang et al. (2010)

(continued)

Table 8.2 (continued)

Microorganism(s)	Leaching mechanism	T°C	pH	Reactor type	Pulp density (*w*/*v*)	Leached metals (percentage, mg/g printed circuit boards)	References
Chromobacterium violaceum, *Pseudomonas aeruginosa*	Complexolysis (CN^-)	30 °C	9.2	Batch reactor	1%	**Cu** 83% (105 mg/g), **Zn** 49% (27 mg/g), **Au** 73% (0.01 mg/g), **Ag** 8% (0.03 mg/g)	Pradhan and Kumar (2012)
Pseudomonas chlororaphis	Complexolysis (CN^-)	25 °C	7.0	Batch reactor	1.6%	**Au** (8%), **Ag** (12%), **Cu** (52%)	Ruan et al. (2014)
A. ferrooxidans, *A. thiooxidans*, *Thiobacillus denitrificans*, *Thiobacillus thioparus*, *Bacillus subtilis*, *Bacillus cereus*	Acidolysis (H_2SO_4), redoxolysis (Fe^{3+}), complexolysis (surfactants)	22–37 °C	5.0–7.0	Batch reactor	1%	**Cu** 53% (22 mg/g), **Ni** 48.5% (6.4 mg/g), **Zn** 48% (6 mg/g)	Karwowska et al. (2014)
A. caldus, *Leptospirillum ferriphilum*, *Sulfobacillus benefaciens*, *Ferroplasma acidiphilum*	Acidolysis (H_2SO_4), redoxolysis (Fe^{3+})	37 °C	1.7	Batch reactor	1%	**Cu** 99% (29 mg/g)	Bryan et al. (2015)
A. ferrivorans, *A. thiooxidans*	Acidolysis (H_2SO_4), redoxolysis (Fe^{3+})	23 °C	1.0–2.0	Batch reactor	1%	**Cu** 98% (164 mg/g)	Chen et al. (2015)
Sulfobacillus thermosulfidooxidans, *Thermoplasma acidophilum*	Acidolysis (H_2SO_4), redoxolysis (Fe^{3+})	45 °C	1.5–2.7	Column reactor	n/a (10 kg)	**Cu** 86% (76 mg/g), **Zn** 80% (71 mg/g), **Ni** 74% (15 mg/g), **Al** 64% (6.5 mg/g)	Ilyas et al. (2010)
A. ferrooxidans, *A. thiooxidans*	Acidolysis (H_2SO_4), redoxolysis (Fe^{3+})	28 °C	1.1–1.6	CSTR	1%	**Cu** 99% (151 mg/g)	Mäkinen et al. (2015)
S. thermosulfidooxidans	Acidolysis (H_2SO_4), redoxolysis (Fe^{3+})	45 °C	2.0	CSTR	1.5–3.5%	**Cu** 95% (105 mg/g), **Al** 91% (19 mg/g), **Zn** 96% (18 mg/g), **Ni** 94% (18 mg/g)	Ilyas and Lee (2014b)
A. ferrooxidans	Redoxolysis (Fe^{3+})	30 °C	2.0	Column + CSTR	0.4–1.6%	**Cu** 92% (582 mg/g), **Zn**, 90% (37 mg/g) **Al**, and 59% (41 mg/g)	Nie et al. (2015a)
A. ferrooxidans	Redoxolysis (Fe^{3+})	30 °C	2.0	Batch reactor	1.2%	**Cu** 96% (604 mg/g)	Nie et al. (2014)

A. ferrooxidans showed a lower Cu mobilization efficiency from printed circuit boards when the contact of bacterial cells and the crushed electronic waste was prevented by a selective membrane (Silva et al. 2015).

The Cu mobilization rate primarily depends on the initial pH, Fe^{2+} concentration and oxidation rate of Fe^{2+} to Fe^{3+} ions generated by iron oxidizers (Xiang et al. 2010). The biogenic Fe^{3+} concentration is correlated with the metal mobilization rate and leaching efficiency (Zhu et al. 2011). This confirms the involvement of the indirect leaching mechanism by sulphuric acid (H_2SO_4) and ferric iron (Fe^{3+}) in mobilizing metals. On the other hand, the involvement of the contact mechanism, i.e. the physical attachment of the bacterial cells to the electronic waste material, is strongly mediated by the ionic strength of the solution. *A. ferrooxidans* cells do not attach randomly to the solid surface, but chemotaxis could be involved in the preferential attachment of bacteria (Rohwerder et al. 2003). The interaction between *A. ferrooxidans* cells and crushed printed circuit boards particles is favourable only if the van der Waals attractive force exceeds the electrostatic repulsive force. This greatly depends on the ionic strength of the solution.

The involvement of both contact and non-contact mechanisms was shown, where the final fraction of Cu mobilised was significantly lower (25%) in a system where the contact mechanism was avoided: ground printed circuit board samples of particle size 500–1000 μm were placed inside a semi-permeable Molecular Weight Cut Off (MWCO) membrane-partition system to study the effect of the contact-leaching mechanism on the final leaching efficiency (Fig. 8.3). The main finding was that the bacterial adhesion is responsible for the higher Cu extraction rate. The results for bacterial adhesion tests were consistent with the Derjaguin-Landau-Verwey-Overbeek theory which explains the aggregation of aqueous dispersions and describes the force between charged surfaces interacting within a liquid medium (Silva et al. 2015). It combines the effects of the Van der Waals attraction

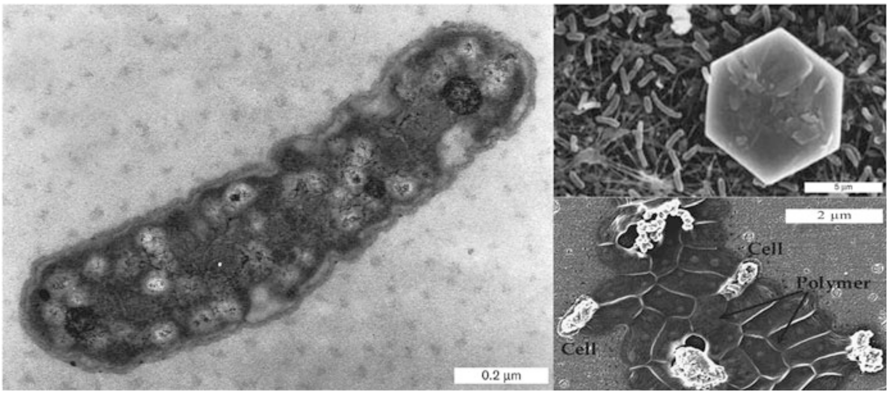

Fig. 8.3 TEM micrographs of single cell *Acidithiobacillus ferrooxidans* (**a**), bioleaching of copper and iron from molybdenite (MoS_2) ore (**b**) and attached to pyrite surface surrounded by polymer (**c**) (Sources: **a**: Mur and Mur 2014; **b**, **c**: Edwards et al. 2000)

and the electrostatic repulsion due to the so-called double layer of counter-ions. It was shown that 24% of the total cells (4.3×10^7 per gram) were attached on printed circuit boards in the initial 60 min. Bacterial attachment evidently plays a crucial role in the Cu extraction efficiency from printed circuit boards. Furthermore, a decrease in the oxidation-reduction potential (ORP) was observed when bacterial contact was avoided. The higher ORP value of the contact conditions over non-contact conditions suggests that the oxidation of Fe^{2+} by the attached bacteria occurs (Silva et al. 2015).

It has been speculated that the mechanism of Cu leaching from printed circuit boards by *A. ferrooxidans* is similar to that of metal sulphides (Ilyas et al. 2010). It may involve indirect leaching mechanisms by the biogenic sulphuric acid, where the role of the microorganisms is to oxidize elemental sulphur (S^0) to sulphuric acid (H_2SO_4). Ferrous iron (Fe^{2+}) in the aqueous solution plays a role as electron donor, and is oxidized to ferric iron (Fe^{3+}) by the iron-oxidizers. Biogenic Fe^{3+} then acts as an oxidizing agent as shown in Eq. (8.5) catalysing the leaching reaction. This translates into a combined acidolysis-redoxolysis bioleaching mechanism for metal dissolution from waste materials, as shown in Eqs. (8.4) and (8.5):

$$4Fe^{2+} + O_2 + 2H^+ \rightarrow 4Fe^{3+} + 2OH^- \text{(bacterial)} \tag{8.4}$$

$$S^0 + 1.5O_2 + H_2O \rightarrow 2H^+ + SO_4^{2-} \text{(bacterial)} \tag{8.5}$$

Biogenic Fe^{3+} and H_2SO_4 mobilises Cu from electronic waste material as shown, respectively, in Eqs. (8.6) and (8.7).

$$Cu^0 + 2Fe^{3+} \rightarrow Cu^{2+} + 2Fe^{2+} \text{(chemical)} \tag{8.6}$$

$$Cu^0 + 2H^+ + SO_4^{2-} + 0.5O_2 \rightarrow Cu^{2+} + SO_4^{2-} + H_2O \text{(chemical)} \tag{8.7}$$

The metal removal efficiency reportedly decreases significantly with increasing pulp density. This has several possible causes. Firstly, the waste material has an alkaline nature, and therefore is acid-consuming (Brandl et al. 2001). This results in a high pH environment, where the acidophiles do not thrive. Secondly, the non-metallic organic fraction, i.e. epoxy-coated substrate, of the material can be toxic to the bacteria (Niu and Li 2007; Zhu et al. 2011).

8.2.5 Bioleaching Microorganisms

8.2.5.1 Microorganisms Involved in Bioleaching

Bioleaching of metals is performed by a diverse group of microorganisms. Indigenous bacteria in natural ores and metal-rich environments grow on the surface of the metal-bearing minerals (Ghauri et al. 2007). A variety of lithotrophic and organotrophic microorganisms mediate the leaching processes (Bharadwaj and Ting 2012). A list of microorganisms involved in bioleaching is given in Table 8.1. Mainly, three groups of microorganisms are classified in bioleaching, namely **(1)** chemolithotrophic prokaryotes, including Bacteria and Archaea, **(2)** heterotrophic bacteria and **(3)** heterotrophic fungi (Johnson and Du Plessis 2015). The majority of the identified acidophiles belongs to the mesophilic and moderately thermophilic bacteria or thermophilic Archaea. Although high temperature processing with thermophiles accelerates the reaction rates (Olson et al. 2003), most full-scale applications are operated at mesophilic temperatures, i.e. below 40 °C (Ilyas and Lee 2015).

Sulphur oxidizers, e.g. *Acidithiobacillus thiooxidans,* generate sulphuric acid (acidolysis) which results in leaching of metals. Iron oxidisers, e.g. *Leptospirillum ferrooxidans* are involved in the production of biogenic ferric iron (redoxolysis), which is a powerful oxidizer bringing the metals to their ionic form in solution. Several soil bacteria and fungi excrete complexing compounds, e.g. cyanide and form chelates (complexolysis). The major microorganisms that are found in bioleaching environments belong to the genera *Acidimicrobium*, *Acidisphaera*, *Acidithiobacillus*, *Acidobacterium*, *Acidocella*, *Acidiphilium*, *Alicyclobacillus*, *Ferrimicrobium*, *Frateuria*, *Leptospirillum*, *Sulfobacillus*, and *Thiomonas*.

Acidophiles are able to readily adapt to extreme conditions (Hedrich et al. 2011), which is also observable in their vast genetic variation among many strains (Kimura et al. 2011). The full genome of several strains of bioleaching microorganisms such as *A. ferrooxidans* (Valdés et al. 2008a), *Metallosphaera sedula* (Auernik et al. 2008) and cyanide producing *Pseudomonas putida* (Canovas et al. 2003) were sequenced, which gave an insight into the genes enabling bioleaching mechanisms, heavy metal resistance and cell-metal interactions. Moreover, gene modification of the well-studied organism *Chromobacterium violaceum* has been experimented to enhance the microbes ability to produce metal complexing metabolites (Natarajan et al. 2015b).

8.2.5.2 Chemolithoautotrophs

8.2.5.2.1 Chemolithotrophs Involved in Bioleaching of Metals

Certain groups of prokaryotes, called the chemolithotrophs, obtain their energy from the oxidation of reduced inorganic compounds. The majority of acidophilic bioleaching organisms are autotrophs that use inorganic carbon (CO_2) as their carbon source (Donati and Sand 2007). They derive energy from the oxidation of inorganic compounds such as ferrous iron (Fe^{2+}) or reduced sulphur compounds, such as elemental sulphur (S^0) and metal sulphides (MeS). Some species also derive energy from the oxidation of hydrogen gas under aerobic or anaerobic conditions (Hedrich and Johnson 2013). Most chemolithoautotrophs have a high tolerance for heavy metals (Orell et al. 2010). *Acidithiobacillus ferrooxidans, Acidithiobacillus thiooxidans* and *Leptospirillum ferrooxidans* are the most extensively studied mesophilic microbes in bioleaching communities. There is an increasing interest in thermophilic chemolithoautotrophic bioleaching with involvement of microorganisms such as *Acidianus brierleyi*, *Sulfobacillus thermosulfidooxidans* and *Metallosphaera sedula* (Du Plessis et al. 2007). These acidophiles grow on iron- and sulphur-containing mining ores such as pyrite (FeS_2), pentlandite ($(Fe,Ni)_9S_8$) and chalcopyrite ($CuFeS_2$) at temperatures in the range of 45–75 °C.

8.2.5.2.2 Genus *Acidithiobacillus*

The genus *Acidithiobacillus* belongs to the γ-proteobacteria and has been considered as one of the most important groups of microorganisms in biomining. These bacteria are obligate acidophilic, gram-negative rods with an average of 0.4 × 2.0 μm in size (Fig. 8.4), motile by one or more flagella and use iron and sulphur for autotrophic growth. They exhibit very high genetic variation (Kimura et al. 2011). Many species, formerly known as *Thiobacillus,* including *Thiobacillus thiooxidans,* and *Thiobacillus caldus,* as well as *Thiobacillus ferrooxidans*, were reassigned to the genus *Acidithiobacillus* on the basis of physiological characteristics and 16S rRNA gene-sequence comparisons (Kelly and Wood 2000). In particular, the bacterium *Acidithiobacillus ferrooxidans* is a major microbe in bioleaching communities (Johnson and Hallberg 2003). This species plays an important role in the biogeochemical cycling of metals in the environment, being involved in solubilising minerals and also immobilising metal cations (Gadd 2010). As with many other chemolithotrophs, their ability to oxidise Fe^{2+}, and less

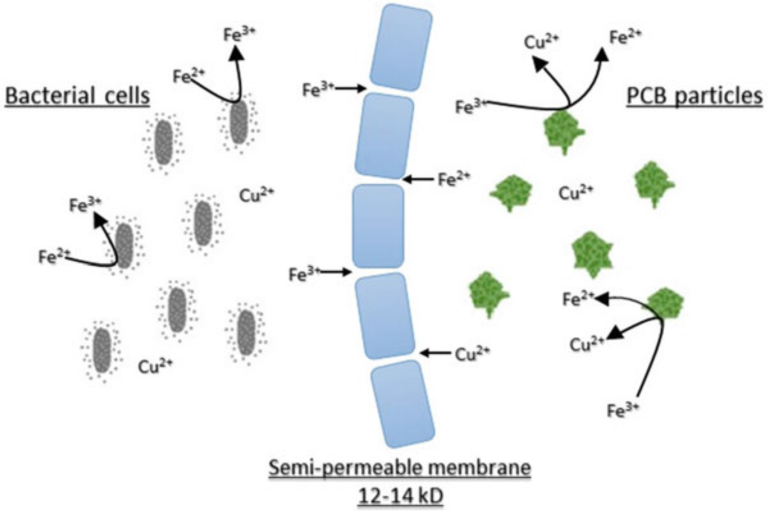

Fig. 8.4 Bacterial adhesion model by *Acidithiobacillus ferrooxidans* on crushed printed circuit board (PCB) in bioleaching (Redrawn from Silva et al. 2015)

commonly S^0, is the key characteristic of the species of the genus *Acidithiobacillus*. These bacteria are abundant in natural environments associated with pyritic ore bodies, coal deposits, and acid mine drainages. Many strains are potentially agents to extract and recover metals, as well as to assist in bioremediation applications. Research work on autotrophic mesophilic bioleaching of metals from waste materials, more specifically discarded printed circuit boards, has focused on the species of the genus *Acidithiobacillus*, especially *A. ferrooxidans* and *A. thiooxidans* (Wang et al. 2009; Hong and Valix 2014).

A. ferrooxidans is one of the few microorganisms known to gain energy by the oxidation of ferrous iron in acidic environments, generating reverse electron flow from Fe^{2+} to NADH (Yin et al. 2014a). Its importance in industrial applications led to complete sequencing of the genome (Valdés et al. 2008a). The iron and sulphur oxidation mechanisms, nutrient uptake, heavy metal resistance mechanisms, biofilm formation, quorum sensing, inorganic ion uptake of this microorganism are explained in detail by Valdés et al. (2008a). *A. thiooxidans* is a mesophilic obligate aerobe that couples the oxidation of elemental sulphur and a variety of reduced sulphur compounds to sulphate, coupled with production of protons. It is one of the first isolated acidophilic microorganism in 1922 by Waksman and Joffe (Bosecker 1997).

8.2.5.3 Heterotrophs

8.2.5.3.1 Organic Acid-Producing Heterotrophs

Members of the organic acid- and complexant-producing bacterial genera *Bacillus*, *Pseudomonas*, *Chromobacterium* as well as fungal genera *Aspergillus, Penicillium* have been extensively studied in bioleaching. Compared to acidophiles, heterotrophs tolerate a wider pH range and are employed for treating moderately alkaline wastes (Natarajan et al. 2015a). Research work on heterotrophic bioleaching of metals from waste materials has been focused on the cyanide- and organic acid-generating microorganisms. Heterotrophic bacteria and fungi are involved in bioleaching with microbial production of organic acids (Bosecker 1997). Organic acids play a role as bioleaching agents (Brandl 2008). Also, other metabolites could play a role as leaching agents for extraction of metals from waste material. In most cases of heterotrophic bioleaching, organic acids directly solubilize metals (Gadd 2000).

8.2.5.3.2 Cyanide-Producing Heterotrophs

Cyanide is a secondary metabolite formed by oxidative decarboxylation of glycine (NH_2CH_2COOH) as shown in Eq. (8.8). It is typically formed only during the early stationary phase, and in certain growth media. Cyanide has an ecological role, e.g. suppressing diseases on plant roots (Bakker et al. 2007). Induction of the genes (*hcn*) involved in cyanide production is initiated under oxygen limitation conditions. However, some species are known to produce considerable amounts of cyanide under normal conditions (Blumer and Haas 2000).

$$NH_2CH_2COOH \rightarrow HCN + CO_2 + 2H_2 \tag{8.8}$$

Biological production of cyanide by bacteria depends on several fundamental parameters such as precursor concentration (i.e. glycine), initial pH, operating temperature, presence of waste material/ore, and oxygen concentration (Fairbrother et al. 2009; Shin et al. 2013). Of the above-listed parameters, precursor concentration and pH have a narrow optimum range. Glycine is essential for biogenic cyanide production. However, high concentrations of glycine is reported to be inhibitory for growth (Castric 1977). Cyanide is chemically stable at high pH, and gold cyanidation is most efficient in the pH range of 10.5–11. However, a pH higher than 9.5 is inhibitory for cell growth of most cyanogenic bacteria (Liang et al. 2014). A few studies investigated the adaptation of cyanogenic bacteria to pH values above 9.5 so as to promote the leaching efficiency (Ting and Pham 2009; Natarajan and Ting 2014). *Chromobacterium violaceum*, which is the most widely studied cyanogenic heterotroph despite several strains being opportunistic pathogens, can adapt to pH values up to 9.5. Adapted cells enabled an increase of the bioleaching efficiency owing to increased chemical stability of CN^- under alkaline conditions.

The genus *Pseudomonas* encompasses some of the most well-studied and versatile heterotrophs in biotechnology in a wide field of applications. A number of strains such as *P. aeruginosa*, *P. fluorescens* and *P. putida* are commonly utilized in bioleaching of metals. They are ubiquitous microbes, typically found in soil biota, and significant in bioleaching due to their various metabolites. Cyanide is optimally excreted during growth limitation and may provide the microbe, which is usually cyanide-tolerant, a selective advantage (Kaksonen et al. 2014). Cyanide production occurs in the rhizosphere where a potential symbiotic relationship between the plants and the cyanide excreting microorganisms is speculated (Ubalua 2010). Biological Au solubilization is a complexolysis reaction between Au and biogenic cyanide (Fairbrother et al. 2009). Gold recovery by *Pseudomonas* is experimented by many researchers on primary ores (Shin et al. 2013) and crushed WEEE (Pradhan and Kumar 2012; Işildar et al. 2016). Several strategies including sequential nutrient addition (Brandl et al. 2008), genetic modification (Natarajan et al. 2015b), and medium modification (Natarajan and Ting 2015) have been developed to increase the cyanide production of the microorganisms.

8.2.5.3.3 Fungi

Fungal bioleaching occurs through acidolysis and redoxolysis mechanisms, involving citric acid, oxalic acid and gluconic acid (Deng et al. 2013). These acids induce the leaching of metals from ores and waste materials by regulating redox potential and acidity (Ubaldini et al. 1998; Gadd 2010). In contrast to acidophilic bacterial leaching, fungal bioleaching takes place at a relatively higher pH (9.0–10.5) (Xu and Ting 2004). *Aspergillus niger* and *Penicillium simplicissimum* are among the most used fungi in bioleaching of metals from waste materials (Lee and Pandey 2012). In the presence of WEEE, they are able to adapt to high pulp densities up to 10% (*w*/*v*) in about 5–6 weeks (Brandl et al. 2001).

8.2.6 Bioreactors

Bioprocessing of metals from primary ores has developed into a successful technique with a number of full scale reactors currently being operated (Brierley and Brierley 2013). An increasing amount of the global Cu production, around 20%, is carried out by bioleaching plants (Schlesinger et al. 2011). Moreover, biooxidation of refractory concentrates, mostly of Au ores, is a well-established full scale process which takes place in tank reactors (Acevedo 2000). However, for the secondary materials, such as WEEE, it is still at its infancy. Recent studies focused on increasing the waste load rate in reactors, and prevention of the toxic effects of electronic waste on the bacteria.

Ilyas et al. (2007) investigated column bioleaching of Al, Cu, Ni, and Zn from crushed printed circuit boards by moderately thermophilic acidophilic chemolithotrophic and heterotrophic consortia. After an adaptation period of 27 days, they reached a final leaching efficiency of 64%, 86%, 74%, and 80%, for Al, Cu, Ni, and Zn, respectively. Follow-up studies by the same research group in a continuous stirred reactor (CSTR) bioleaching setup using a moderately thermophilic adapted culture of *Sulfobacillus thermosulfidooxidans* resulted in a 91%, 95%, 94%, and 96% leaching efficiency for Al, Cu, Ni, and Zn, respectively, at a pulp density of 10% (*w*/*v*). The CSTR was supplemented with 25% oxygen (O_2) and 0.03% carbon dioxide (CO_2), along with 2.5% (*w*/*v*) biogenic S^0 and maintained at 45 °C. An interesting finding was the faster oxidation rate of the biogenic over the technical S^0. Conclusively it was attributed to the higher bioavailability and hydrophobicity of biogenic S^0 (Ilyas and Lee 2014b).

In their study, Mäkinen et al. (2015) reported the bioleaching of Cu from a low-grade printed circuit board (153 mg Cu/g printed circuit board) in a CSTR. The bioleaching medium consisted of 10 g/L S^0 and the initial Fe^{2+} concentration was varied to investigate the effect of this electron donor on the final bioleaching efficiency. The sulphur-oxidizers dominated the microbial consortium over iron-oxidizers as a result of pre-cultivation procedure without adding the Cu-rich waste material. The pre-cultivation produced a bioleaching solution with pH 1.1, Fe^{3+} concentration of 7.4 g/L (Fe^{2+} concentration was 0.4 g/L) and redox potential of +655 mV.

The pH increased with the addition of pre-treated PCB, due to the alkaline nature of the material (Brandl et al. 2001). The pH was maintained at around 1.6 by sulphuric acid (95% *v*/*v* H_2SO_4) addition. A fluctuation redox potential (between +290 and 655 mV) and pH (between 1.1 and 2.6) was observed. Following an initial decrease of Fe^{2+} due to bacterial oxidation, an increase up to 6.8 g/L was observed which indicated a cyclic reaction of Fe^{2+}/Fe^{3+}. 99% of Cu was bioleached in 3 days with optimal initial Fe^{2+} concentration (9 g/L). Cu and Fe were the only major cations in the final bio-leachate solution, with a maximal concentration of 6.8 and 9 g/L, respectively, of Cu and Fe (Mäkinen et al. 2015).

Chen et al. (2015) experimented the bioleaching of Cu by *Acidithiobacillus ferrooxidans* from crushed PC printed circuit board (248 mg Cu/g printed circuit board). They used a standard bioleaching medium (4.5 K) containing about 6 g/L Fe $^{2+}$. The pH was controlled by H_2SO_4 addition. After bioleaching for 28 days in the column setup the Cu recovery was 94.8%. As similar to Mäkinen et al. (2015), they maintained the pH in an acidic range (up to 1.8) with dilute H_2SO_4 addition to prevent iron hydrolysis and jarosite formation which can decrease the bioleaching efficiency. This hybrid chemical/biological approach enables the coupled cyclic Fe $^{2+}$-Fe^{3+} reaction and creates optimal conditions for Cu bioleaching.

Nie et al. (2015a) bioleached 96% of the Cu from discarded printed circuit boards (602 mg Cu/g printed circuit board) extracted from metal concentrates by an *A.ferrooxidans*-dominated mixed culture in 7 days in a combined CSTR reactor. At an initial Fe^{2+} concentration of 12 g/L, the acidophilic bacterial consortium was able to demonstrate an average ferrous oxidation rate of 0.2307 g L/h. Protons produced by the ionization of sulphuric acid (acidolysis) and the hydrolysis of Fe^{3+} played only a slight role in the extraction of Cu. Dialysis bag experiments show 81.4% of Cu was leached out by bioleaching without dialysis bag compared with 47.9% in the encapsulated bioleaching system. The extraction of Cu was mainly through the indirect oxidation process (redoxolysis) via biogenic Fe^{3+} by *A. ferrooxidans*. Both contact and non-contact mechanisms led to the dissolution of Cu from discarded printed circuit boards.

Despite its many advantages, bioleaching of waste material for metal recovery has several constraints. Bioleaching processes are limited by several factors such as lengthy leaching periods up to 15 days as well as toxic effects of the waste material on the microorganisms. There is vast potential for process optimization, particularly with the optimization of the biological reactions. Recent studies showed that a metal leaching efficiency of 99% could be achieved with improved kinetics (3 days) at relatively high pulp densities of 10% (*w*/*v*). Bacteria can tolerate conditions previously considered to be highly toxic after an adaptation period in the reactor set-up. Further engineering of this property allows development of novel biotechnological processes in the context of bioprocessing of electronic waste for metal recovery.

8.3 Biorecovery of Metals

Many well-practised conventional techniques, including solvent extraction, cementation, ion exchange, precipitation, adsorption, and electrowinning, enable selective recovery of metals from leachate solutions (Table 8.3). They are used to selectively recover As, Cd, Se, Cu, Fe, Ni, Zn, Cr, and Pb from domestic (Fu and Wang 2011) and industrial wastewater (González-Muñoz et al. 2006) and solid wastes (Cui and Zhang 2008; Tuncuk et al. 2012). There is also an increasing interest on bio-sorbents for precious metal recovery from aqueous solutions (Das 2010). Several biological processes, such as biosorption, bioreduction, biomineralisation, and bioprecipitation can be alternative metal recovery methods (Hennebel et al. 2015). The selection of an appropriate technique for metal recovery depends on process parameters, such as the metal concentration in the leachate liquor and metal-selective behaviour of the selected technique. At industrial scale, many recovery processes are a combination of the above-mentioned conventional techniques (Schlesinger et al. 2011).

Currently, research on selective recovery of metals from electronic waste leachate liquors is limited. Compared to primary ores, electronic waste materials are very concentrated in metals and complex owing to the prevalence of a large number of metals (Ongondo et al. 2015). Use of biomass-based techniques for the recovery of metals is an emerging field with vast potential. Biorecovery of metals from electronic waste could provide a viable, environmentally friendly option (Gadd 2010). Several mechanisms of cation removal by microbial cells are proposed, such as **(i)** binding on cell surfaces, **(ii)** resistance/detoxification mechanisms, **(iii)** bioaccumulation within the cell wall, **(iv)** active translocation inside the cell through metal binding proteins, and **(v)** mineralisation processes such as the interaction with extracellular polymers, or volatilisation (Das 2010; Andrès and Gérente 2011). In this section, biosorption, bioreduction, biomineralisation and bioprecipitation from aqueous solutions are overviewed.

Table 8.3 Overview of metal biorecovery techniques

Biorecovery mechanism	Targeted metals	References
Biosorption	Precious metals: Ag, Au, Pd, Pt	Vijayaraghavan et al. (2011), Park et al. (2010), Mikheenko et al. (2008) and Xie et al. (2003)
Reductive bioprecipitation	Precious metals: Au, Pd, Pt	Kashefi et al. (2001) and Creamer et al. (2006)
Biomineralisation	Cu and precious metals: Cu, Au, Pd	Reith et al. (2009) and Johnston et al. (2013)
Bioprecipitation (sulphide)	Base metals: Cu, Ni, Zn	Cao et al. (2009), Sahinkaya et al. (2009), Sampaio et al. (2009) and Janyasuthiwong et al. (2015)

8.3.1 Biosorption

Biosorption is a feature of microbial biomass to bind and concentrate metals from aqueous solutions. On a cellular scale, biosorption takes place at the cell wall or by various metabolites, e.g. metal-binding peptides, polysaccharides, extracellular polymeric substances (EPS) (Gadd 2010). The chemical functional groups of the cell wall play a vital role in biosorption (Ilyas and Lee 2014a). Several functional groups are present on the cell wall including carboxyl, phosphoryl, amine and hydroxyl groups (Wang and Chen 2009). Carboxylic groups of the cell wall peptidoglycan of the Actinobacteria *Streptomyces pilosus* are responsible for the binding of divalent metal ions (Tunca et al. 2007). Other bio-sorbents include compounds with a relatively high surface amine functional group content. This is generally due to the ability of the positively charged amine groups to attract metal ions (Mack et al. 2007). Recently, Tanaka and Watanabe (2015) spectroscopically showed that Pt was absorbed on bacterial cells and formed a four-fold coordination of chlorine ions, similar to Pt_4^{2-} using X-ray absorption fine structure spectroscopy (XAFS), which indicated that sorption occurs on the protonated amine groups of the bacterial cells. Pt^{4+} was reduced to Pt^{2+} on the cell's surface, even in the absence of an organic material as an exogenous electron donor.

Algae, fungi, yeasts, and bacteria play a role as biosorbent for precious metals (Mack et al. 2007). An overview of sorption of precious metals is given below in Table 8.4. Active cells of the green alga *Chlorella vulgaris* have a high efficiency in removing Au from solution (Ting and Mittal 2002). The brown alga *Sargassum natans* is highly selective towards Au (Das 2010). Inactivated cells of the related species *Fucus vesiculosus* can recover elemental Au as nanoparticles (Mata et al. 2009). The fungal cells of *Aspergillus niger*, *Mucor rouxii* and *Rhizopus arrihus* were found to take up gold along with other precious metals (Syed 2012). Two strains of the fungus *Cladosporium cladosporioides* showed preferential sorption of Au (Pethkar et al. 2001). Among the gram-negative bacteria, *Acinetobacter calcoaceticus, Erwinia herbicola, Pseudomonas aeruginosa* and *Stenotrophomonas maltophilia* are capable of Au biosorption (Das 2010; Ye et al. 2013). It is a viable alternative for metal recovery from dilute solutions (Mack et al. 2007; Wang and Chen 2009).

8.3.2 Reductive Bioprecipitation

Reductive bioprecipitation describes enzymatically assisted metal precipitation from a positive valence to a zero-valent state (Rawlings et al. 2003). Bioreduction of metals takes place either by direct contact to the cell surface or through extracellular electron shuttles (Manzella et al. 2013). Biomineral formation takes place through a number of mechanisms, e.g. bioprecipitation, intracellular

Table 8.4 Biosorption of precious metals from aqueous solutions by algal, bacterial, and fungal cells

Metal	Biosorbent	Mode of action	Uptake (mg/g biomass)	T°C	pH	References
Algae						
Au(III)	*Sargassum natans*	Inactive biomass	82.7	Ambient	7.0	Kuyucak and Volesky (1988)
Au(III)	*Chlorella vulgaris*	Inactive cells	98.5	Ambient	2.0	Darnall et al. (1986)
Au(III)	*Turbinaria conoide*	Inactive cells	34.5	25 °C	2.0	Vijayaraghavan et al. (2011)
Au(Cl_4^-)	*Fucus vesiculosus*	Inactive cells	75	Ambient	7.0	Mata et al. (2009)
Au(CN_2^-)	*Bacillus subtilis*	Inactive biomass	92.5	Ambient	2.0	Niu and Volesky (2000)
Ag(II)	*Bacillus cereus*	Inactive biomass	91.4	30 °C	4.0	Li et al. (2011)
Bacteria						
Au(III)	*Escherichia coli*	Active cells	115	Ambient	6.5	Deplanche and Macaskie (2008)
Au(CN_2^-)	*Corynebacterium glutamicum*	Inactive cells	421.1	25 °C	5.5	Park et al. (2012)
Pd(II)	*Delsufovibrio desulfuricans*	Active cells	190.0	37 °C	3.0	de Vargas et al. (2004)
Pd(II)	*Desulfovibrio fructosivorans*	Active cells	63.8	37 °C	2.3	Mikheenko et al. (2008)
Pd(II)	*Escherichia coli*	Inactive cells	265.3	25 °C	3.0	Park et al. (2010)
Pd(II)	*Corynebacterium glutamicum*	Active cells	176.8	25 °C	2.0	Won et al. (2011)
Pd(II)	*Escherichia coli*	Inactive biomass	265.3	25 °C	3.0	Won et al. (2010)
Pt(II)	*Escherichia coli*	Inactive biomass	108.8	25 °C	Acidic	Won et al. (2010)
Pt(II)	*Bacillus subtilis*	Active cells	100.0	25 °C	2.0	Tanaka and Watanabe (2015)
Pt(IV)	*Shewanella putrefaciens*	Active cells	100.0	25 °C	4.0	Tanaka and Watanabe (2015)
Pt(IV)	*Delsufovibrio desulfuricans*	Active cells	90.0	37 °C	3.0	de Vargas et al. (2004)

(continued)

Table 8.4 (continued)

Metal	Biosorbent	Mode of action	Uptake (mg/g biomass)	T°C	pH	References
Fungi						
Au(III)	*Fomitopsis carnea*	Inactive cells	94.3	25 °C	8.0	Khoo and Ting (2001)
Au(III)	*Cladosporium cladosporioides*	Biomass beads	101.0	Ambient	4.0	Pethkar et al. (2001)
Au(III)	*Aspergillus niger*	Active cells	197.0	Ambient	7.0	Kuyucak and Volesky (1988)
Pt(IV)	*Saccharomyces cerevisiae*	Inactive cells	44.0	Ambient	3.5	Xie et al. (2003)

accumulation, nanoparticle formation, bioreduction, or redox immobilization (Gadd 2010).

Enzymatic mechanisms promote metal ion reduction under favourable conditions, independently of cell metabolism. The identification of the enzymatic mechanisms may indicate their prevalence in growth-decoupled activity. In some occasions, metal bioreduction takes place via direct electron transport producing crystals of metal oxides or base metals accumulated on the cell surface (Deplanche et al. 2011). Bacterial biofilms are present on the surface of Au nuggets (Reith et al. 2009), despite the inherently toxic characteristics of soluble Au, the bacterial cells are speculated to accumulate Au intracellularly (Johnston et al. 2013). A number of hyperthermophilic and mesophilic dissimilatory iron-reducing bacteria and archaea are capable of producing precipitates of elemental gold from Au^{3+} cations (Kashefi et al. 2001). Bioreduction of Au^{3+} is an enzymatically catalysed reaction, and dependent on electron donor supply, e.g. hydrogen. Au precipitated extracellularly with much of the elemental Au attached to the outer surface of the cells. The mechanism of reductive precipitation of Au by ferric iron-reducing microorganisms is significantly different from the bioaccumulation of Au (Kashefi et al. 2001).

Selective reductive bioprecipitation of metals from electronic waste leach liquor using *Desulfovibrio desulfuricans* biomass has been investigated in batch tests by Creamer et al. (2006). It proved effective for Au^{3+}, Pd^{2+}, and Cu^{2+} in a three-step process. In the first step, active cells selectively precipitated Au^{3+} to elemental Au^0 from the leach liquor, while Pd^{2+} precipitation was inhibited due the presence of high amounts of Cu^{2+}. In the second step, the pre-treated (palladised) biomass was used to catalyse the conversion of Pd^{2+} as elemental Pd^0. In the third step, the remaining leachate solution was treated by the biogas (not analysed) generated by *Klebsiela pneumoniae* or *Escherichia coli*, where Cu is removed as a mixture of hydroxide and sulphate salts. In the Au and Pd recovery steps, hydrogen sparing enabled the initiation of metal reduction (Creamer et al. 2006). Although the biogas was not analysed for its content, it is known from an earlier work that it included dimethyldisulfide, which is presumably the metal-precipitant in the solution (Essa et al. 2006).

8.3.3 Biomineralisation

Investigations on *Cupriavidus metallidurans* have revealed that it bioaccumulates inert Au nanoparticles within its cytoplasm as a mechanism to protect itself from soluble Au (Fig. 8.5; Reith et al. 2009). The gold-resistant bacterium *Delftia acidovorans* produces a metabolite, namely delftibactin, that assists its survival (Johnston et al. 2013). It is speculated that this bacterium secretes metabolites against toxicity, which in turn enables biomineralisation of elemental Au^0.

Foulkes et al. (2016) demonstrated the presence of a novel mechanism responsible for the biomineralisation of Pd(II) in aerobically grown cultures of *E. coli*, catalysed mainly by molybdenum-containing enzyme systems. The strain that lacked all molybdoenzymes did still reduce the palladium, although within 7 h, compared to less than 30 min by the wild-type strains. The real-time analysis showed that bioPd(0) was mineralized outside the cells. Biomineralisation of platinum group metals (PGMs) from electronic waste is an emerging field of biotechnology. It is a viable alternative for the selective recovery of metals from complex electronic waste leachates containing these precious metals. Moreover, the microbial cells are selective towards individual metals, which gives this technology advantages over conventional technologies.

8.3.4 Biogenic Sulphide Precipitation of Metals

Sulphide precipitation of metals is an established technique, particularly for wastewaters with high metal concentrations, e.g. acid mine drainage. Biotechnological applications of bacterial sulphate reduction have a couple of advantages such as cost-effectiveness and lower volume of sludge generated as compared to hydroxide precipitation. Moreover, they enable selective precipitation of metal sulphides in a

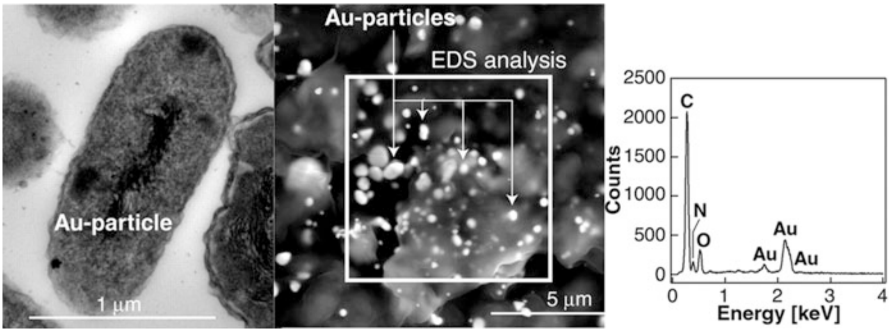

Fig. 8.5 Gold biomineralisation in the bacterium *Cupriavidus metallidurans*; Transmission electron micrograph (TEM) of ultra-thin section containing Au nanoparticle (**a**), Scanning electron microscopy micrograph (SEM) (**b**), with energy dispersive X-ray analysis (EDS) (**c**) (Source: Reith et al. 2009)

pH dependent stoichiometry (Sahinkaya et al. 2009; Sampaio et al. 2010). It attracts scientific interest owing to its advantages such as lower solubility of precipitates, potential for selective metal removal, fast reaction rates, and potential for re-use of metal sulphide precipitates by smelting (Lewis 2010).

Sulphide precipitation can be carried out using either aqueous (Na_2S, NaHS) or gaseous sulphide sources (H_2S). Many studies investigated the removal efficiency, reaction kinetics and crystallization properties (Sahinkaya et al. 2009; Mokone et al. 2010; Janyasuthiwong et al. 2015). The solubility characteristics of metal sulphide compounds enable selective precipitation from a mixed metal solution.

In biogenic sulphidic precipitation, sulphate-reducing bacteria (SRB) oxidize organic compounds by sulphate as an electron acceptor and generate sulphide (S^{2-}) and alkalinity. Reduction of SO_4^{2-} under ambient conditions occurs solely in the presence of microorganisms. In a continuous system, SRB produce hydrogen sulphide in the first reactor and the subsequent metal precipitation takes place in the second reactor (Jong and Parry 2003). This process is based on the ability of SRB to reduce sulphates to sulphides, which form insoluble precipitates of metal sulphides (Lewis 2010). Generic reactions are given in Eqs. (8.9) and (8.10):

$$\text{Organic matter (C, H, O)} + SO_4^{2-} \rightarrow HS^- + HCO_3^- \tag{8.9}$$

$$Me^{2+} + HS^- \rightarrow MeS \downarrow + H^+ \tag{8.10}$$

Cao et al. (2009) investigated the precipitation characteristics of metal cations from a WEEE leachate solution. Metal concentrations of 20, 5, 2, and 0.5 g/L for Mg^{2+}, Fe^{3+}, Ni^{2+} and Cu^{2+}, respectively, were used for sulphidic precipitation with biologically-produced H_2S gas. The sulphide concentration strongly influenced the precipitation efficiency. The Cu removal rate was the highest, followed respectively by Fe, Ni, and Mg. Cu removal was 100% in two experiments with various sulphide concentrations, while Fe removal was 62.7–100% and Ni removal was 46.4–100%. Moreover, the efficiency of metal precipitation with biogenic H_2S depended on the reactor type. The pH had a significant influence on the metal removal since the rate of H_2S dissolution is faster at high pH. The pH of the bioleaching solution had no influence on the precipitation efficiency, provided that the H_2S concentration was sufficient for metal sulphide precipitation (Cao et al. 2009).

8.4 Conclusions

Electronic waste, in particular discarded PCB, is a promising secondary source of metals. Cu is the predominant metal by weight, along with substantial amounts of other base metals and precious metals. Biotechnological metal recovery techniques enable more environmentally friendly and cost-effective processes, and are expected to play a significant role in sustainable development. The composition of bio-leachate solutions from waste materials is very complex, which requires novel strategies to recover metals. Research work on metal recovery from electronic waste has focused on acidophilic and cyanogenic bioleaching processes. A very high (>99%) Cu bioleaching efficiency has been achieved in laboratory scale batch and continuous set-ups. The main influencing operating parameters were pH, redox potential, microbial activity and pulp density. Recent studies showed that the leaching process can be significantly accelerated and the bacteria can process higher loads of WEEE in bioreactors.

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References

Acevedo F (2000) The use of reactors in biomining processes. Electron J Biotechnol 3:184–194. doi:10.2225/vol3-issue3-fulltext-4

Acuna J, Rojas J, Amaro AM, Toledo H, Jerez CA (1992) Chemotaxis of *Leptospirillum ferrooxidans* and other acidophilic chemolithotrophs: comparison with the *Escherichia coli* chemosensory system. FEMS Microbiol Lett 96(1):37–42

Andrès Y, Gérente C (2011) Removal of rare earth elements and precious metal species by biosorption. In: Kotrba P, Mackova M, Macek T (eds) Microbial biosorption of metals. Springer, Dordrecht, pp 179–196

Arundel A, Sawaya D (2009) The bioeconomy to 2030: Designing a policy agenda. OECD - Better Policies for Better Lives. http://www.oecd.org/futures/long-termtechnologicalsocietalchallenges/thebioeconomyto2030designingapolicyagenda.htm

Auernik KS, Maezato Y, Blum PH, Kelly RM (2008) The genome sequence of the metal-mobilizing, extremely thermoacidophilic archaeon *Metallosphaera sedula* provides insights into bioleaching-associated metabolism. Appl Environ Microbiol 74:682–692. doi:10.1128/AEM.02019-07

Bakker PAHM, CMJ P, van Loon LC (2007) Induced systemic resistance by fluorescent *Pseudomonas* spp. Phytopathology 97:239–243. doi:10.1094/PHYTO-97-2-0239

Baldé CP, Wang F, Kuehr R, Huisman J (2015) The global E-waste monitor 2014: quantities, flows, and resources. United Nations University, Bonn

Bas AD, Deveci H, Yazici EY (2013) Bioleaching of copper from low grade scrap TV circuit boards using mesophilic bacteria. Hydrometallurgy 138:65–70. doi:10.1016/j.hydromet.2013.06.015

Bharadwaj A, Ting YP (2012) From biomining of mineral ores to bio urban mining of industrial waste. Environmental Technology and Management Conference, 4th, EMTC, Indonesia

Blumer C, Haas D (2000) Mechanism, regulation, and ecological role of bacterial cyanide biosynthesis. Arch Microbiol 173:170–177

Bonnefoy V, Holmes DS (2012) Genomic insights into microbial iron oxidation and iron uptake strategies in extremely acidic environments. Environ Microbiol 14:1597–1611. doi:10.1111/j.1462-2920.2011.02626.x

Bosecker K (1997) Bioleaching: metal solubilization by microorganisms. FEMS Microbiol Rev 20:591–604. doi:10.1016/S0168-6445(97)00036-3

Brandl H (2008) Microbial leaching of metals. In: Biotechnology set, 2nd edn. Wiley-VCH Verlag GmbH, Weinheim, pp 191–224

Brandl H, Faramarzi M (2006) Microbe-metal-interactions for the biotechnological treatment of metal-containing solid waste. China Particuology 4:93–97. doi:10.1016/S1672-2515(07)60244-9

Brandl H, Bosshard R, Wegmann M (2001) Computer-munching microbes: metal leaching from electronic scrap by bacteria and fungi. Hydrometallurgy 59:319–326. doi:10.1016/S0304-386X(00)00188-2

Brandl H, Lehmann S, Faramarzi MA, Martinelli D (2008) Biomobilization of silver, gold, and platinum from solid waste materials by HCN-forming microorganisms. Hydrometallurgy 94:14–17. doi:10.1016/j.hydromet.2008.05.016

Brasseur G, Levican G, Bonnefoy V, Holmes D, Jedlicki E, Lemesle-Meunier D (2004) Apparent redundancy of electron transfer pathways via bc1 complexes and terminal oxidases in the extremophilic chemolithoautotrophic *Acidithiobacillus ferrooxidans*. Biochim Biophys Acta – Bioenerg 1656:114–126. doi:10.1016/j.bbabio.2004.02.008

Brierley JA, Brierley CL (1986) Microbial mining using thermophilic microorganisms. In: Brock TD (ed) Thermophiles: general, molecular, and applied microbiology. Wiley, New York, pp 279–305

Brierley J, Brierley C (2001) Present and future commercial applications of biohydrometallurgy. Hydrometallurgy 59:233–239. doi:10.1016/S0304-386X(00)00162-6

Brierley CL, Brierley JA (2013) Progress in bioleaching: Part B: applications of microbial processes by the minerals industries. Appl Microbiol Biotechnol 97:7543–7552. doi:10.1007/s00253-013-5095-3

Bryan CG, Watkin EL, McCredden TJ, Wong ZR, Harrison STL, Kaksonen AH (2015) The use of pyrite as a source of lixiviant in the bioleaching of electronic waste. Hydrometallurgy 152:33–43. doi:10.1016/j.hydromet.2014.12.004

Campbell SC, Olson GJ, Clark TR, McFeters G (2001) Biogenic production of cyanide and its application to gold recovery. J Ind Microbiol Biotechnol 26:134–139. doi:10.1038/sj.jim.7000104

Canovas D, Cases I, de Lorenzo V (2003) Heavy metal tolerance and metal homeostasis in *Pseudomonas putida* as revealed by complete genome analysis. Environ Microbiol 5:1242–1256. doi:10.1046/j.1462-2920.2003.00463.x

Cao J, Zhang G, Mao Z, Wu P, Dang Z, Li P, Wu J (2009) Precipitation of valuable metals from bioleaching solution by biogenic sulfides. Miner Eng 22:289–295. doi:10.1016/j.mineng.2008.08.006

Castric PA (1977) Glycine metabolism by *Pseudomonas aeruginosa*: hydrogen cyanide biosynthesis. J Bacteriol 130:826–831

Chen SY, Huang QY (2014) Heavy metals recovery from printed circuit board industry wastewater sludge by thermophilic bioleaching process. J Chem Technol Biotechnol 89:158–164. doi:10.1002/jctb.4129

Chen LX, Hu M, Huang LN, Hua ZS, Kuang JL, Li SJ, Shu WS (2015) Comparative metagenomic and metatranscriptomic analyses of microbial communities in acid mine drainage. ISME J 9(7):1579–1592. doi:10.1038/ismej.2014.245

Clark DA, Norris PR (1996) *Acidimicrobium ferrooxidans* gen nov, sp nov: mixed-culture ferrous iron oxidation with *Sulfobacillus* species. Microbiology 142:785–790. doi:10.1099/00221287-142-4-785

Colmer AR, Hinkle ME (1947) The role of microorganisms in acid mine drainage: a preliminary report. Science 106:253–256. doi:10.1126/science.106.2751.253

Corstjens PLAM, De Vrind JPM, Westbroek P, De Vrind-De Jong EW (1992) Enzymatic iron oxidation by *Leptothrix discophora*: identification of an iron-oxidizing protein. Appl Environ Microbiol 58:450–454

Creamer NJ, Baxter-Plant VS, Henderson J, Potter M, Macaskie LE (2006) Palladium and gold removal and recovery from precious metal solutions and electronic scrap leachates by *Desulfovibrio desulfuricans*. Biotechnol Lett 28:1475–1484. doi:10.1007/s10529-006-9120-9

Cui J, Zhang L (2008) Metallurgical recovery of metals from electronic waste: a review. J Hazard Mater 158:228–256. doi:10.1016/j.jhazmat.2008.02.001

Darland G, Brock TD, Samsonoff W, Conti SF (1970) A thermophilic, acidophilic mycoplasma isolated from a coal refuse pile. Science 170:1416–1418. doi:10.1126/science.170.3965.1416

Darnall DW, Greene B, Henzl MT, Hosea JM, McPherson RA, Sneddon J, Dale AM (1986) Selective recovery of gold and other metal ions from an algal biomass. Environ Sci Technol 20:206–208

Das N (2010) Recovery of precious metals through biosorption – a review. Hydrometallurgy 103:180–189. doi:10.1016/j.hydromet.2010.03.016

de Vargas I, Macaskie LE, Guibal E (2004) Biosorption of palladium and platinum by sulfate-reducing bacteria. J Chem Technol Biotechnol 79:49–56

Del Olmo A, Caramelo C, San Jose C (2003) Fluorescent complex of pyoverdin with aluminum. J Inorg Biochem 97:384–387. doi:10.1016/S0162-0134(03)00316-7

Deng X, Chai L, Yang Z, Tang C, Wang Y, Shi Y (2013) Bioleaching mechanism of heavy metals in the mixture of contaminated soil and slag by using indigenous *Penicillium chrysogenum* strain F1. J Hazard Mater 248–249:107–114. doi:10.1016/j.jhazmat.2012.12.051

Deplanche K, Macaskie LE (2008) Biorecovery of gold by *Escherichia coli* and *Desulfovibrio desulfuricans*. Biotechnol Bioeng 99:1055–1064. doi:10.1002/bit.21688

Deplanche K, Murray A, Mennan C, Scott T, Macaskie L (2011) Biorecycling of precious metals and rare earth elements. InTech, Nanomaterials:279–315. Doi:https://doi.org/10.5772/25653

Donati ER, Sand W (2007) Microbial processing of metal sulfides. Springer, Dordrecht

Du Plessis CA, Batty JD, Dew DW (2007) Commercial applications of thermophile bioleaching. Biomining:57–80. doi:10.1007/978-3-540-34911-2_3

Edwards KJ, Bond PL, Gihring TM, Banfield JF (2000) An archaeal iron-oxidizing extreme acidophile important in acid mine drainage. Science 287:1796–1799. doi:10.1126/science.287.5459.1796

Escobar B, Jedlicki E, Wiertz J, Vargas T (1996) A method for evaluating the proportion of free and attached bacteria in the bioleaching of chalcopyrite with *Thiobacillus ferrooxidans*. Hydrometallurgy 40:1–10. doi:10.1016/0304-386X(95)00005-2

Essa A, Creamer N, Brown N, Macaskie L (2006) A new approach to the remediation of heavy metal liquid wastes via off-gases produced by *Klebsiella pneumoniae* M426. Biotechnol Bioeng 95:574–583. doi:10.1002/bit.20877

Fabisch M, Beulig F, Akob DM, Küsel K (2013) Surprising abundance of *Gallionella*-related iron oxidizers in creek sediments at pH 4.4 or at high heavy metal concentrations. Front Microbiol 4:1–12. doi:10.3389/fmicb.2013.00390

Fairbrother L, Shapter J, Brugger J, Southam G, Pring A, Reith F (2009) Effect of the cyanide-producing bacterium *Chromobacterium violaceum* on ultraflat Au surfaces. Chem Geol 265:313–320. doi:10.1016/j.chemgeo.2009.04.010

Faramarzi M, Stagars M, Pensini E (2004) Metal solubilization from metal-containing solid materials by cyanogenic *Chromobacterium violaceum*. J Biotechnol 113:321–326. doi:10.1016/j.jbiotec.2004.03.031

Foulkes JM, Deplanche K, Sargent F, Macaskie LE, Lloyd JR (2016) A novel aerobic mechanism for reductive palladium biomineralization and recovery by *Escherichia coli*. Geomicrobiol J 33:230–236. doi:10.1080/01490451.2015.1069911

Fu F, Wang Q (2011) Removal of heavy metal ions from wastewaters: a review. J Environ Manag 92:407–418. doi:10.1016/j.jenvman.2010.11.011

Fuchs T, Huber H, Teiner K, Burggraf S, Stetter KO (1995) *Metallosphaera prunae*, sp. nov., a novel metal-mobilizing, thermoacidophilic Archaeum, isolated from a uranium mine in Germany. Syst Appl Microbiol 18:560–566. doi:10.1016/S0723-2020(11)80416-9

Gadd GM (2000) Bioremedial potential of microbial mechanisms of metal mobilization and immobilization. Curr Opin Biotechnol 11(3):271–279

Gadd GM (2010) Metals, minerals and microbes: geomicrobiology and bioremediation. Microbiology 156:609–643. doi:10.1099/mic.0.037143-0

Gadd SA, Joffe JS (1922) Microörganisms concerned in the oxidation of sulfur in the soil. J Bacteriol 7:239–256. doi:10.1097/00010694-192205000-00002.

Ghauri MA, Okibe N, Johnson DB (2007) Attachment of acidophilic bacteria to solid surfaces: the significance of species and strain variations. Hydrometallurgy 85:72–80. doi:10.1016/j.hydromet.2006.03.016

Golovacheva RS, Karavaiko GI (1978) New genus of thermophilic spore-forming bacteria, Sulfobacillus. Microbiology 47(5):658–665

Golyshina OV, Pivovarova TA, Karavaiko GI, Kondrat'eva TF, Moore ERB, Abraham WR, Lünsdorf H, Timmis KN, Yakimov MM, Golyshin PN (2000) *Ferroplasma acidiphilum* gen. nov., sp. nov., an acidophilic, autotrophic, ferrous-iron-oxidizing, cell-wall-lacking, mesophilic member of the *Ferroplasmaceae* fam. nov., comprising a distinct lineage of the Archaea. Int J Syst Evol Microbiol 50:997–1006. doi:10.1099/00207713-50-3-997

González-Muñoz MJ, Rodríguez MA, Luque S, Álvarez JR (2006) Recovery of heavy metals from metal industry waste waters by chemical precipitation and nanofiltration. Desalination 200:742–744. doi:10.1016/j.desal.2006.03.498

Habashi F (2005) A short history of hydrometallurgy. Hydrometallurgy 79:15–22. doi:10.1016/j.hydromet.2004.01.008

Hadi P, Xu M, Lin CSK, Hui CW, McKay G (2015) Waste printed circuit board recycling techniques and product utilization. J Hazard Mater 283:234–243. doi:10.1016/j.jhazmat.2014.09.032

Hawkes RB, Franzmann PD, O'hara G, Plumb JJ (2006) *Ferroplasma cupricumulans* sp. nov., a novel moderately thermophilic, acidophilic Archaeon isolated from an industrial-scale chalcocite bioleach heap. Extremophiles 10:525–530. doi:10.1007/s00792-006-0527-y

Hedrich S, Johnson DB (2013) Aerobic and anaerobic oxidation of hydrogen by acidophilic bacteria. FEMS Microbiol Lett 349:40–45. doi:10.1111/1574-6968.12290

Hedrich S, Schlömann M, Johnson DB (2011) The iron-oxidizing proteobacteria. Microbiology 157:1551–1564. doi:10.1099/mic.0.045344-0

Hennebel T, Boon N, Maes S, Lenz M (2015) Biotechnologies for critical raw material recovery from primary and secondary sources: R&D priorities and future perspectives. N Biotechnol 32:121–127. doi:10.1016/j.nbt.2013.08.004

Hong Y, Valix M (2014) Bioleaching of electronic waste using acidophilic sulfur oxidising bacteria. J Clean Prod 65:465–472. doi:10.1016/j.jclepro.2013.08.043

Huber G, Spinnler C, Gambacorta A, Stetter KO (1989) *Metallosphaera sedula* gen, and sp. nov. represents a new genus of aerobic, metal-mobilizing, thermoacidophilic archaebacteria. Syst Appl Microbiol 12:38–47. doi:10.1016/S0723-2020(89)80038-4

Ilyas S, Lee JC (2014a) Biometallurgical recovery of metals from waste electrical and electronic equipment: a review. ChemBioEng Rev 1:148–169. doi:10.1002/cben.201400001

Ilyas S, Lee JC (2014b) Bioleaching of metals from electronic scrap in a stirred tank reactor. Hydrometallurgy 149:50–62. doi:10.1016/j.hydromet.2014.07.004

Ilyas S, Lee JC (2015) Bioprocessing of electronic scraps. In: Abhilash PBD, Natarajan KA (eds) Microbiology for minerals, metals, Materials and the environment. CRC Press, Boca Raton, pp 307–328. https://doi.org/10.1201/b18124-13

Ilyas S, Anwar MA, Niazi SB, Ghauri MA (2007) Bioleaching of metals from electronic scrap by moderately thermophilic acidophilic bacteria. Hydrometallurgy 88:180–188. doi:10.1016/j.hydromet.2007.04.007

Ilyas S, Ruan C, Bhatti HN, Ghauri MA, Anwar MA (2010) Column bioleaching of metals from electronic scrap. Hydrometallurgy 101:135–140. doi:10.1016/j.hydromet.2009.12.007

Ishigaki T, Nakanishi A, Tateda M, Ike M, Fujita M (2005) Bioleaching of metal from municipal waste incineration fly ash using a mixed culture of sulfur-oxidizing and iron-oxidizing bacteria. Chemosphere 60:1087–1094. doi:10.1016/j.chemosphere.2004.12.060

Işildar A, van de Vossenberg J, Rene ER, van Hullebusch ED, Lens PNL (2016) Two-step bioleaching of copper and gold from discarded printed circuit boards (PCB). Waste Manag 57:149–157. doi:10.1016/j.wasman.2015.11.033

Jan RL, Wu J, Chaw SM, Tsai CW, Tsen SD (1999) A novel species of thermoacidophilic archaeon, *Sulfolobus yangmingensis* sp. nov. Int J Syst Bacteriol 49(Pt 4):1809–1816. doi:10.1099/00207713-49-4-1809

Janyasuthiwong S, Rene ER, Esposito G, Lens PNL (2015) Effect of pH on Cu, Ni and Zn removal by biogenic sulfide precipitation in an inversed fluidized bed bioreactor. Hydrometallurgy 158:94–100. doi:10.1016/j.hydromet.2015.10.009

Johnson DB, Bacelar-Nicolau P, Okibe N, Thomas A, Hallberg KB (2009) *Ferrimicrobium acidiphilum* gen. nov., sp. nov. and *Ferrithrix thermotolerans* gen. nov., sp. nov.: heterotrophic, iron-oxidizing, extremely acidophilic actinobacteria. Int J Syst Evol Microbiol 59:1082–1089. doi:10.1099/ijs.0.65409-0

Johnson DB, Hallberg KB (2003) The microbiology of acidic mine waters. Res Microbiol 154:466–473. doi:10.1016/S0923-2508(03)00114-1

Johnson DB, Du Plessis CA (2015) Biomining in reverse gear: using bacteria to extract metals from oxidised ores. Miner Eng 75:2–5. doi:10.1016/j.mineng.2014.09.024

Johnston CW, Wyatt MA, Li X, Ibrahim A, Shuster J, Southam G, Magarvey N (2013) Gold biomineralization by a metallophore from a gold-associated microbe. Nat Chem Biol 9:241–243. doi:10.1038/nchembio.1179

Jong T, Parry DL (2003) Removal of sulfate and heavy metals by sulfate reducing bacteria in short-term bench scale upflow anaerobic packed bed reactor runs. Water Res 37:3379–3389. doi:10.1016/S0043-1354(03)00165-9

Kaksonen AH, Mudunuru BM, Hackl R (2014) The role of microorganisms in gold processing and recovery–a review. Hydrometallurgy 142:70–83. doi:10.1016/j.hydromet.2013.11.008

Karwowska E, Andrzejewska-Morzuch D, Łebkowska M, Tabernacka A, Wojtkowska M, Telepko A, Konarzewska A (2014) Bioleaching of metals from printed circuit boards supported with surfactant-producing bacteria. J Hazard Mater 264:203–210. doi:10.1016/j.jhazmat.2013.11.018

Kashefi K, Tor JM, Nevin KP, Lovley DR (2001) Reductive precipitation of gold by dissimilatory Fe (III)-reducing bacteria and archaea. Appl Environ Microbiol 67:3275–3279. doi:10.1128/AEM.67.7.3275

Kelly DP, Wood AP (2000) Reclassification of some species of *Thiobacillus Acidithiobacillus* gen. nov., *Halothiobacillus* gen. nov. and *Thermithiobacillus* gen. nov. Int J Syst Evol Microbiol 50:511–516

Khoo KM, Ting YP (2001) Biosorption of gold by immobilized fungal biomass. Biochem Eng J 8:51–59. doi:10.1016/S1369-703X(00)00134-0

Kimura S, Bryan CG, Hallberg KB, Johnson DB (2011) Biodiversity and geochemistry of an extremely acidic, low-temperature subterranean environment sustained by chemolithotrophy. Environ Microbiol 13:2092–2104. doi:10.1111/j.1462-2920.2011.02434.x

Knowles CJ (1976) Microorganisms and cyanide. Bacteriol Rev 40:652–680

Kozubal MA, Dlakić M, Macur RE, Inskeep WP (2011) Terminal oxidase diversity and function in "*Metallosphaera yellowstonensis*": gene expression and protein modeling suggest mechanisms of Fe(II) oxidation in the *Sulfolobales*. Appl Environ Microbiol 77:1844–1853. doi:10.1128/AEM.01646-10

Kuyucak N, Volesky B (1988) Biosorbents for recovery of metals from industrial solutions. Biotechnol Lett 10:137–142. doi:10.1007/BF01024641

Lee J, Pandey B (2012) Bio-processing of solid wastes and secondary resources for metal extraction-a review. Waste Manag 32:3–18. doi:10.1016/j.wasman.2011.08.010

Leff LG, Ghosh S, Johnston GP, Roberto A (2015) Microbial remediation of acid mine drainage. In: Abhilash PBD, Natarajan KA (eds) Microbiology for minerals, metals, materials and the environment. CRC Press, Boca Raton, pp 453–475. https://doi.org/10.1201/b18124-19

Lewis AE (2010) Review of metal sulphide precipitation. Hydrometallurgy 104:222–234. doi:10.1016/j.hydromet.2010.06.010

Li L, Hu Q, Zeng J, Qi H, Zhuang G (2011) Resistance and biosorption mechanism of silver ions by *Bacillus cereus* biomass. J Env Sci 23:108–111. doi:10.1016/S1001-0742(10)60380-4

Liang G, Mo Y, Zhou Q (2010) Novel strategies of bioleaching metals from printed circuit boards (PCBs) in mixed cultivation of two acidophiles. Enzyme Microb Technol 47:322–326. doi:10.1016/j.enzmictec.2010.08.002

Liang CJ, Li JY, Ma CJ (2014) Review on cyanogenic bacteria for gold recovery from E-waste. Adv Mater Res 878:355–367. doi:10.4028/www.scientific.net/AMR.878.355

Liu YG, Zhou M, Zeng GM, Li X, Xu WH, Fan T (2007) Effect of solids concentration on removal of heavy metals from mine tailings via bioleaching. J Hazard Mater 141:202–208. doi:10.1016/j.jhazmat.2006.06.113

Mack C, Wilhelmi B, Duncan JR, Burgess JE (2007) Biosorption of precious metals. Biotechnol Adv 25:264–271. doi:10.1016/j.biotechadv.2007.01.003

Mäkinen J, Bachér J, Kaartinen T, Wahlström M, Salminen J (2015) The effect of flotation and parameters for bioleaching of printed circuit boards. Miner Eng 75:26–31. doi:10.1016/j.mineng.2015.01.009

Manzella MP, Reguera G, Kashefi K (2013) Extracellular electron transfer to Fe(III) oxides by the hyperthermophilic archaeon *Geoglobus ahangari* via a direct contact mechanism. Appl Environ Microbiol 79:4694–4700. doi:10.1128/AEM.01566-13

Mapelli F, Marasco R, Balloi A, Rolli E, Cappitelli F, Daffonchio D, Borin S (2012) Mineral-microbe interactions: biotechnological potential of bioweathering. J Biotechnol 157:473–481. doi:10.1016/j.jbiotec.2011.11.013

Mata YN, Torres E, Blázquez ML, Ballester A, González F, Muñoz JA (2009) Gold(III) biosorption and bioreduction with the brown alga *Fucus vesiculosus*. J Hazard Mater 166:612–618. doi:10.1016/j.jhazmat.2008.11.064

Melamud VS, Pivovarova TA, Tourova TP, Kolganova TV, Osipov GA, Lysenko AM, Kondrat'eva TF, Karavaiko GI (2003) *Sulfobacillus sibiricus* sp. nov., a new moderately thermophilic bacterium. Microbiology 72:605–612. doi:10.1023/A:1026007620113

Mikheenko IP, Rousset M, Dementin S, Macaskie LE (2008) Bioaccumulation of palladium by *Desulfovibrio fructosivorans* wild-type and hydrogenase-deficient strains. Appl Environ Microbiol 74:6144–6146. doi:10.1128/AEM.02538-07

Mishra A, Pradhan N, Kar RN, Sukla LB, Mishra BK (2009) Microbial recovery of uranium using native fungal strains. Hydrometallurgy 95:175–177. doi:10.1016/j.hydromet.2008.04.005

Mishra D, Rhee YH (2014) Microbial leaching of metals from solid industrial wastes. J Microbiol 52:1–7. doi:10.1007/s12275-014-3532-3

Mokone TP, van Hille RP, Lewis AE (2010) Effect of solution chemistry on particle characteristics during metal sulfide precipitation. J Colloid Interface Sci 351:10–18. doi:10.1016/j.jcis.2010.06.027

Murr LE, Murr LE (2014) Structure and function of viruses and bacteria. In: Handbook of materials structures, properties, processing and performance. Springer, Cham, pp 1–14

Natarajan G, Ting YP (2014) Pretreatment of e-waste and mutation of alkali-tolerant cyanogenic bacteria promote gold biorecovery. Bioresour Technol 152:80–85. doi:10.1016/j.biortech.2013.10.108

Natarajan G, Ting YP (2015) Gold biorecovery from e-waste: an improved strategy through spent medium leaching with pH modification. Chemosphere 136:232–238. doi:10.1016/j.chemosphere.2015.05.046

Natarajan G, Ramanathan T, Bharadwaj A (2015a) Bioleaching of metals from major hazardous solid wastes. Microbiol Miner Met Mater Environ 2025:229–262

Natarajan G, Tay SB, Yew WS, Ting YP (2015b) Engineered strains enhance gold biorecovery from electronic scrap. Miner Eng 75:32–37. doi:10.1016/j.mineng.2015.01.002

Neilands JB (1995) Siderophores: structure and function of microbial iron transport compounds. J Biol Chem 270:26723–26726. doi:10.1074/jbc.270.45.26723

Nemati M, Harrison STL (2000) Comparative study on thermophilic and mesophilic biooxidation of ferrous iron. Miner Eng 13:19–24. doi:10.1016/S0892-6875(99)00146-6

Nie S, Yao S, Qin C, Li K, Liu X, Wang L, Song X, Wang S (2014) Kinetics of AOX formation in chlorine dioxide bleaching of bagasse pulp. BioResources 9(3):5604–5614. http://ncsu.edu/bioresources. ISSN: 1930–2126

Nie H, Yang C, Zhu N, Wu P, Zhang T, Zhang Y, Xing Y (2015a) Isolation of *Acidithiobacillus ferrooxidans* strain Z1 and its mechanism of bioleaching copper from waste printed circuit boards. J Chem Technol Biotechnol 90:714–721. doi:10.1002/jctb.4363

Nie H, Zhu N, Cao Y, Xu Z, Wu P (2015b) Immobilization of *Acidithiobacillus ferrooxidans* on cotton gauze for the bioleaching of waste printed circuit boards. Appl Biochem Biotechnol 177:675–688. doi:10.1007/s12010-015-1772-2

Niu H, Volesky B (2000) Gold-cyanide biosorption with L-cysteine. J Chem Technol Biotechnol 75:436–442. doi:10.1002/1097-4660(200006)75:6<436::AID-JCTB243>3.0.CO;2-O

Niu X, Li Y (2007) Treatment of waste printed wire boards in electronic waste for safe disposal. J Hazard Mater 145:410–416. doi:10.1016/j.jhazmat.2006.11.039

Olson GJ, Brierley JA, Brierley CL (2003) Bioleaching review part B: progress in bioleaching: applications of microbial processes by the minerals industries. Appl Microbiol Biotechnol 63:249–257. doi:10.1007/s00253-003-1404-6

Ongondo FO, Williams ID, Whitlock G (2015) Distinct urban mines: exploiting secondary resources in unique anthropogenic spaces. Waste Manag 45:4–9. doi:10.1016/j.wasman.2015.05.026

Orell A, Navarro CA, Arancibia R, Mobarec JC, Jerez CA (2010) Life in blue: copper resistance mechanisms of bacteria and archaea used in industrial biomining of minerals. Biotechnol Adv 28:839–848. doi:10.1016/j.biotechadv.2010.07.003

Park J, Won SW, Mao JE, Kwak IS, Yun YS (2010) Recovery of Pd(II) from hydrochloric solution using polyallylamine hydrochloride-modified *Escherichia coli* biomass. J Hazard Mater 181:794–800. doi:10.1016/j.jhazmat.2010.05.083

Park SI, Kwak IS, Bae MA, Mao J, Won SW, Han DH, Chung YS, Yun YS (2012) Recovery of gold as a type of porous fiber by using biosorption followed by incineration. Bioresour Technol 104:208–214. doi:10.1016/j.biortech.2011.11.018

Pethkar AV, Kulkarni SK, Paknikar KM (2001) Comparative studies on metal biosorption by two strains of *Cladosporium cladosporioides*. Bioresour Technol 80:211–215. doi:10.1016/S0960-8524(01)00080-3

Plumb JJ, Gibbs G, Stott MB, Robertson WJ, Gibson JAE, Nichols PD, Watling HR, Franzmann PD (2002) Enrichment and characterization of thermophilic acidophiles for the bioleaching of mineral sulphides. Miner Eng 15:787–794, https://doi.org/10.1016/S0892-6875(02)00117-6

Plumb JJ, McSweeney NJ, Franzmann PD (2008) Growth and activity of pure and mixed bioleaching strains on low grade chalcopyrite ore. Miner Eng 21:93–99. doi:10.1016/j.mineng.2007.09.007

Potysz A, Lens PNL, van de Vossenberg J, Rene ER, Grybos M, Guibaud G, Kierczak J, van Hullebusch ED (2016) Comparison of Cu, Zn and Fe bioleaching from Cu-metallurgical slags in the presence of *Pseudomonas fluorescens* and *Acidithiobacillus thiooxidans*. Appl Geochem 68:39–52. doi:10.1016/j.apgeochem.2016.03.006

Pradhan JK, Kumar S (2012) Metals bioleaching from electronic waste by *Chromobacterium violaceum* and *Pseudomonads* sp. Waste Manag Res 30:1151–1159. doi:10.1177/0734242X12437565

Rawlings DE (2005) Characteristics and adaptability of iron- and sulfur-oxidizing microorganisms used for the recovery of metals from minerals and their concentrates. Microb Cell Fact 4:13. doi:10.1186/1475-2859-4-13

Rawlings DE, Johnson DB (2007) The microbiology of biomining: development and optimization of mineral-oxidizing microbial consortia. Microbiology 153:315–324. doi:10.1099/mic.0.2006/001206-0

Rawlings DE, Dew D, Du Plessis C (2003) Biomineralization of metal-containing ores and concentrates. Trends Biotechnol 21:38–44. doi:10.1016/S0167-7799(02)00004-5

Rees KL, van Deventer JSJ (1999) Role of metal-cyanide species in leaching gold from a copper concentrate. Miner Eng 12:877–892. doi:10.1016/S0892-6875(99)00075-8

Reith F, Etschmann B, Grosse C, Moors H, Benotmane MA, Monsieurs P, Grass G, Doonan C, Vogt S, Lai B, Martinez-Criado G, George GN, Nies DH, Mergeay M, Pring A, Southam G, Brugger J (2009) Mechanisms of gold biomineralization in the bacterium *Cupriavidus metallidurans*. Proc Natl Acad Sci USA 106:17757–17762. doi:10.1073/pnas.0904583106

Rohwerder T, Gehrke T, Kinzler K, Sand W (2003) Bioleaching review part A: progress in bioleaching: fundamentals and mechanisms of bacterial metal sulfide oxidation. Appl Microbiol Biotechnol 63:239–248. doi:10.1007/s00253-003-1448-7

Ruan J, Zhu X, Qian Y, Hu J (2014) A new strain for recovering precious metals from waste printed circuit boards. Waste Manag 34:901–907. doi:10.1016/j.wasman.2014.02.014

Sahinkaya E, Gungor M, Bayrakdar A, Yucesoy Z, Uyanik S (2009) Separate recovery of copper and zinc from acid mine drainage using biogenic sulfide. J Hazard Mater 171:901–906. doi:10.1016/j.jhazmat.2009.06.089

Sampaio RMM, Timmers RA, Xu Y, Keesman KJ, Lens PNL (2009) Selective precipitation of Cu from Zn in a pS controlled continuously stirred tank reactor. J Hazard Mater 165:256–265. doi:10.1016/j.jhazmat.2008.09.117

Sampaio RMM, Timmers RA, Kocks AV, Duarte MT, Van Hullebusch ED, Farges F, Lens PNL (2010) Zn-Ni sulfide selective precipitation: the role of supersaturation. Sep Purif Technol 74:108–118. doi:10.1016/j.seppur.2010.05.013

Sand W, Rohde K, Sobotke B, Zenneck C (1992) Evaluation of *Leptospirillum ferrooxidans* for leaching. Appl Environ Microbiol 58:85–92

Sand W, Gehrke T, Jozsa PG, Schippers A (2001) (Bio)chemistry of bacterial leaching – direct vs. indirect bioleaching. Hydrometallurgy 59:159–175. doi:10.1016/S0304-386X(00)00180-8

Schippers A, Jozsa PG, Sand W (1996) Sulfur chemistry in bacterial leaching of pyrite. Appl Environ Microbiol 62:3424–3431

Schlesinger ME, King MJ, Sole KC, Davenport WG (2011) Extractive metallurgy of copper, 5th edn. Elsevier, Oxford

Shin D, Jeong J, Lee S, Pandey BD, Lee JC (2013) Evaluation of bioleaching factors on gold recovery from ore by cyanide-producing bacteria. Miner Eng 48:20–24. doi:10.1016/j.mineng.2013.03.019

Silva RA, Park J, Lee E, Park J, Choi SQ, Hyunjungal K (2015) Influence of bacterial adhesion on copper extraction from printed circuit boards. Sep Purif Technol 143:169–176. doi:10.1016/j.seppur.2015.01.038

Silverman MP, Lundgren DG (1959) Studies on the chemoautotrophic iron bacterium *Ferrobacillus ferrooxidans*. J Bacteriol 78:326–331

Spolaore P, Joulian C, Gouin J, Morin D, D'Hugues P (2011) Relationship between bioleaching performance, bacterial community structure and mineralogy in the bioleaching of a copper concentrate in stirred-tank reactors. Appl Microbiol Biotechnol 89:441–448. doi:10.1007/s00253-010-2888-5

Syed S (2012) Recovery of gold from secondary sources – a review. Hydrometallurgy 115–116:30–51. doi:10.1016/j.hydromet.2011.12.012

Tanaka K, Watanabe N (2015) Study on the coordination structure of Pt sorbed on bacterial cells using X-ray absorption fine structure spectroscopy. PLoS One 10:1–12. doi:10.1371/journal.pone.0127417

Tay SB, Natarajan G, Rahim MNBA, Tan HT, Chung MC, Ming T, Yen P, Yew WS (2013) Enhancing gold recovery from electronic waste via lixiviant metabolic engineering in *Chromobacterium violaceum*. Sci Rep 3:2236. doi:10.1038/srep02236

Ting Y, Mittal AK (2002) Effect of pH on the biosorption of gold by a fungal biosorbent. Resour Environ Biotechnol 3:229–239. http://scholarbank.nus.edu.sg/handle/10635/66550

Ting Y, Pham V (2009) Gold bioleaching of electronic waste by cyanogenic bacteria and its enhancement with bio-oxidation. Adv Mater Res 73:661–665. doi:10.4028/www.scientific.net/AMR.71-73.661

Tributsch H (2001) Direct versus indirect bioleaching. Hydrometallurgy 59:177–185. doi:10.1016/S0304-386X(00)00181-X

Tunca S, Barreiro C, Sola-Landa A, Coque JJR, Martín JF (2007) Transcriptional regulation of the desferrioxamine gene cluster of *Streptomyces coelicolor* is mediated by binding of DmdR1 to an iron box in the promoter of the desA gene. FEBS J 274:1110–1122. doi:10.1111/j.1742-4658.2007.05662.x

Tuncuk A, Stazi V, Akcil A, Yazici EY, Deveci H (2012) Aqueous metal recovery techniques from e-scrap: hydrometallurgy in recycling. Miner Eng 25:28–37. doi:10.1016/j.mineng.2011.09.019

Ubaldini S, Fornari P, Massidda R, Abbruzzese C (1998) An innovative thiourea gold leaching process. Hydrometallurgy 48:113–124. doi:10.1016/S0304-386X(97)00076-5

Ubalua A (2010) Cyanogenic glycosides and the fate of cyanide in soil. Aust J Crop Sci 4:223–237

Valdés J, Pedroso I, Quatrini R, Dodson RJ, Tettelin H, Blake R, Eisen JA, Holmes DS (2008a) *Acidithiobacillus ferrooxidans* metabolism: from genome sequence to industrial applications. BMC Genomics 9:597. doi:10.1186/1471-2164-9-597

Valdés J, Pedroso I, Quatrini R, Holmes DS (2008b) Comparative genome analysis of *Acidithiobacillus ferrooxidans, A. thiooxidans* and *A. caldus*: insights into their metabolism and ecophysiology. Hydrometallurgy 94:180–184. doi:10.1016/j.hydromet.2008.05.039

van de Vossenberg JLCM, Driessen AJM, Zillig W, Konings WN (1998) Bioenergetics and cytoplasmic membrane stability of the extremely acidophilic, thermophilic archaeon Picrophilus oshimae. Extremophiles 2:67–74. doi:10.1007/s007920050044

Vera M, Schippers A, Sand W (2013) Progress in bioleaching: fundamentals and mechanisms of bacterial metal sulfide oxidation – Part A. Appl Microbiol Biotechnol 97:7529–7541. doi:10.1007/s00253-013-4954-2

Vijayaraghavan K, Mahadevan A, Sathishkumar M, Pavagadhi S, Balasubramanian R (2011) Biosynthesis of Au(0) from Au(III) via biosorption and bioreduction using brown marine alga *Turbinaria conoides*. Chem Eng J 167:223–227. doi:10.1016/j.cej.2010.12.027

Wang J, Chen C (2009) Biosorbents for heavy metals removal and their future. Biotechnol Adv 27:195–226. doi:10.1016/j.biotechadv.2008.11.002

Wang J, Bai J, Xu J, Liang B (2009) Bioleaching of metals from printed wire boards by *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* and their mixture. J Hazard Mater 172:1100–1105. doi:10.1016/j.jhazmat.2009.07.102

Wang F, Ruediger K, Daniel A, Jinhui L (2013) E-waste in China: a country report. http://collections.unu.edu/eserv/UNU:6132/e_waste_china_en.pdf

Watling HR (2006) The bioleaching of sulphide minerals with emphasis on copper sulphides – a review. Hydrometallurgy 84:81–108. doi:10.1016/j.hydromet.2006.05.001

Watling HR (2015) Review of biohydrometallurgical metals Extraction from polymetallic mineral resources. Minerals 5:1–60. doi:10.3390/min5010001

Won SW, Mao J, Kwak IS, Sathishkumar M, Yun YS (2010) Platinum recovery from ICP wastewater by a combined method of biosorption and incineration. Bioresour Technol 101:1135–1140. doi:10.1016/j.biortech.2009.09.056

Won SW, Park J, Mao J, Yun YS (2011) Utilization of PEI-modified *Corynebacterium glutamicum* biomass for the recovery of Pd(II) in hydrochloric solution. Bioresour Technol 102:3888–3893. doi:10.1016/j.biortech.2010.11.106

Xiang Y, Wu P, Zhu N, Zhang T, Liu W (2010) Bioleaching of copper from waste printed circuit boards by bacterial consortium enriched from acid mine drainage. J Hazard Mater 184:812–818. doi:10.1016/j.jhazmat.2010.08.113

Xie D, Liu Y, Wu CL, Chen P, Fu JK (2003) Studies of properties on the immobilized *Saccharomyces cerevisiae* waste biomass adsorbing Pt. J Xiamen Univ Nat Sci 42(6):800–804

Xie X, Xiao S, He Z, Liu J, Qiu G (2007) Microbial populations in acid mineral bioleaching systems of Tong Shankou Copper Mine, China. J Appl Microbiol 103:1227–1238. doi:10.1111/j.1365-2672.2007.03382.x

Xu TJ, Ting YP (2004) Optimisation on bioleaching of incinerator fly ash by Aspergillus niger–use of central composite design. Enzym Microb Technol 35(5):444–454, https://doi.org/10.1016/j.enzmictec.2004.07.003

Xu TJ, Ting YP (2009) Fungal bioleaching of incineration fly ash: metal extraction and modeling growth kinetics. Enzyme Microb Technol 44:323–328. doi:10.1016/j.enzmictec.2009.01.006

Yang X, Sun L, Xiang J, Hu S, Su S (2013) Pyrolysis and dehalogenation of plastics from waste electrical and electronic equipment (WEEE): a review. Waste Manag 33:462–473. doi:10.1016/j.wasman.2012.07.025

Ye J, Yin H, Xie D, Peng H, Huang J, Liang W (2013) Copper biosorption and ions release by *Stenotrophomonas maltophilia* in the presence of benzo[a]pyrene. Chem Eng J 219:1–9. doi:10.1016/j.cej.2012.12.093

Yin H, Zhang X, Li X, He Z, Liang Y, Guo X, Hu Q, Xiao Y, Cong J, Ma L, Niu J, Liu X (2014a) Whole-genome sequencing reveals novel insights into sulfur oxidation in the extremophile *Acidithiobacillus thiooxidans*. BMC Microbiol 14:179. doi:10.1186/1471-2180-14-179

Yin NH, Sivry Y, Avril C, Borensztajn S, Labanowski J, Malavergne V, Lens PNL, Rossano S, van Hullebusch ED (2014b) Bioweathering of lead blast furnace metallurgical slags by *Pseudomonas aeruginosa*. Int Biodeterior Biodegrad 86:372–381. doi:10.1016/j.ibiod.2013.10.013

Yong P, Rowson NA, Farr JPG, Harris IR, Macaskie LE (2002) Bioreduction and biocrystallization of palladium by *Desulfovibrio desulfuricans* NCIMB 8307. Biotechnol Bioeng 80:369–379. doi:10.1002/bit.10369

Yue G, Guezennec AG, Asselin E (2016) Extended validation of an expression to predict ORP and iron chemistry: application to complex solutions generated during the acidic leaching or bioleaching of printed circuit boards. Hydrometallurgy 164:334–342. doi:10.1016/j.hydromet.2016.06.027

Zammit CM, Cook N, Brugger J, Ciobanu CL, Reith F (2012) The future of biotechnology for gold exploration and processing. Miner Eng 32:45–53. doi:10.1016/j.mineng.2012.03.016

Zhou QG, Bo F, Bo ZH, Xi L, Jian G, Fei FL, Hua CX (2007) Isolation of a strain of *Acidithiobacillus caldus* and its role in bioleaching of chalcopyrite. World J Microbiol Biotechnol 23:1217–1225. doi:10.1007/s11274-007-9350-6

Zhu N, Xiang Y, Zhang T, Wu P, Dang Z, Li P, Wu J (2011) Bioleaching of metal concentrates of waste printed circuit boards by mixed culture of acidophilic bacteria. J Hazard Mater 192:614–619. doi:10.1016/j.jhazmat.2011.05.062

Zimmerley SR, Wilson DG, Prater JD (1958) Cyclic leaching process employing iron oxidising bacteria. US Patent 2:829–964