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Minerals Characterization and Their Applications

Edited by Gonzalo Montes-Atenas

Current Research on Mineralogy - Minerals Characterization and Their Applications

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Aims and Scope of the Series

The world of Earth Sciences, considering the interactions within the geosphere and between the geosphere–biosphere, is a place in which a large number of scientists find and have found over time their own relationship or sector of application precisely because it is absolutely transversal to many disciplines and subdisciplines, which do not necessarily fall within the Geosciences. The objective of this book series is to welcome original scientific contributions both in consolidated contexts and in new frontiers of research, as well as review papers included in the various disciplines of Earth Sciences, but above all, those that show a modern and transversal vision of applications and impacts on the community in a particular historical context, which, following the COVID-19 pandemic, has shifted global attention to sectors that were previously more neglected. In particular, those of mining research and fossil and renewable energy sources, environmental geology and the sustainable use of natural resources and impacts on the built environment, land consumption, geoarchaeology, forensic geology, geotourism/geoheritage, georisks and climate and environmental changes, considered at different scales, up to new applications of geostatistical and geospatial analysis, GIS and artificial intelligence for the definition of forecasting models and scenarios in various sectors of basic and applied research.

Meet the Series Editor

Dr. Maurizio Lazzari has a Ph.D. in Earth Science and is a researcher at the Italian National Research Council, Institute of Cultural Heritage Sciences. Since 2001, Dr. Lazzari has been a Professor of Pedology at the University of Basilicata (Italy) and a geoarchaeologist at the University of Salento (Italy). His research activities are focused on natural and anthropic hazards and risk factors, aimed at safeguarding and conserving settlements and the historical–monumental heritage of the Mediterranean, with particular attention to landslide processes, susceptibility maps, monitoring, and modelling. Since 2004, he has been working as a scientific coordinator for several national research projects studying landslides and triggering factors, natural and anthropogenic risks, geological and geomorphological mapping, soil erosion, preservation of historical and archaeological sites, enhancement of degraded areas, geo-touristic use, and the protection of the landscapes. He is the author of about 150 scientific publications in national and international journals, monographs, book chapters, and conference proceedings concerning applied geology, geomorphology, dynamics of artificial reservoirs, soil erosion, landslides, geoarchaeology, hydrogeological instability, natural hazards, monitoring, cultural landscape, UNESCO Heritage, geoarchaeology, and geo-tourism.

Meet the Volume Editor

Dr. Gonzalo Montes-Atenas obtained a Chemical Engineer diploma from the University of Chile (1994-2000). Then, in 2002, he moved to France, where he obtained a Doctorate in Geosciences in 2004 with a thesis entitled: "Rôle de l'état de surface du fer métallique sur le mécanisme et la cinétique de decomposition de colorants azoiques/ Role of composition and structure of oxidation surface layer of iron in decomposition of differently structured azo-dyes kinetics and reaction pathways" supervised by Professor Jerzy Mielczarski, at the "Pole de l'Eau" belonging to the Institut National Polytechnique de Lorraine (INPL). Afterwards, he worked at Química Rhenium (Chile) as a Research and Innovation Engineer, developing emulsions and foaming agents. In 2006, he held a Marie Curie Fellowship position at the University of Manchester's Chemical Engineering and Analytical Sciences (CEAS) Department. After that, he also held the position of Associate Researcher at the Corrosion and Protection Centre. Later, he held a Research Fellow position at the University of Queensland, specifically at the Julius Kruttschnitt Mineral Research Centre (JKMRC) between 2008 and 2011, where he worked under the supervision of Professor Dee Bradshaw in the P9 AMIRA project on Bubble Loading at an industrial scale. After that, he took an academic position at the Department of Mining Engineering (University of Chile, Chile), where he currently holds the position of Associate Professor, lecturing courses such as Metallurgical Physical Chemistry and Transport Phenomena. Since 2024, he has also served as Research, Development, and Innovation Manager at Empirica Spa (Chile), a leading consulting company specializing in the mining industry worldwide.

Contents

Preface

Mineralogy is undoubtedly a beacon among all branches of science devoted to the study of minerals. The classic definition of the concept of mineralogy, though meaningful, is at this stage an understatement, as it has evolved and nowadays entails, among other subjects, knowledge that is currently translated into many technologies and innovations our society urgently requires.

This book aims to gather relevant information about the practical aspects of working with minerals, while also highlighting current and unresolved challenges. Topics such as the economic production of critical elements and studies focused on the environment, strategically oriented towards developing different strategies for designing wastewater treatment plants and carbon mineralization using minerals, are also presented.

Other contributions range from assessing classic analytical techniques to new trends in the development of spectroscopic techniques, including those that attempt to capture information about mediators formed at the surface of unstable minerals under aerated conditions.

Additionally, this book gathers industrial case studies, which are expected to provide information to undergraduate, postgraduate, and scholars aiming to improve our best practices and reconcile our current knowledge with what society and the environment require, taking us to another level where sustainability is the key.

We want to thank all the authors who have contributed to this book for their efforts in gathering information, discussing it, and presenting the best lines of thought to move forward.

I wish all current and future researchers the very best in their endeavors and hope this book contributes to their success to some extent.

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Section 1

Mineral Characterization and Applications for Mineral Processing and Extractive Metallurgy

Chapter 1

Surface Mineralogy: A Brief Review on the "Mediator" Concept and Some Challenges at the Edge of the Metallurgical Knowledge

Gonzalo Montes-Atenas

Abstract

The concept of mineralogy, originally defined as a geological science focused on the study of minerals within the Earth's crust, encompasses all measurable characteristics of these materials. Significant progress has been made in understanding physical properties such as hardness and roughness. However, knowledge of surface chemical composition and its relationship to surface reactivity remains limited, particularly in systems where metal sulphides play an important role. It is well established that the composition of a bulk solid often bears little resemblance to that observed at a solid-fluid interface. This discrepancy poses major challenges for mineral systems, as determining and quantifying the correct elemental and "mineral" composition of an interface is difficult, even in relatively simple situations such as the exposure of sulphide minerals to atmospheric conditions. In such cases, complex and frequently non-stoichiometric surface structures may form, making them difficult to define and interpret. This chapter seeks to describe some of these scenarios, highlighting the role of so-called "mediators," which are ultimately responsible for mineral surface reactivity. The analytical techniques used to characterise these mediators are shown to be crucial for interpreting their influence. For example, QEMSCAN and XPS analyses applied to the same chalcopyrite sample demonstrate that the depth of analysis is critical. The observation that iron species dominate the outermost surface during oxidation supports qualitative models previously proposed by other authors. In addition, this chapter discusses challenges associated with mineral processing and extractive metallurgy and concludes by outlining potential trends and approaches to address these issues.

Keywords: surface chemistry, hydrometallurgy, mineral processing, mineral surface composition, mediator

1. Introduction

Whenever a heterogeneous chemical reaction occurs in a system bearing a solid phase, the common description appears insufficient to explain all the details involved in the process. Indeed, a chemical reaction usually considers the participation of the bulk phases without considering the actual composition of the interface which is, in fact, the structure promoting or inhibiting the reaction or any other complex process taking place. This has been particularly proven in the case of electrochemical reactions for oxygen reduction on metals, one of the most relevant reactions in industrial processes related to minerals separation and metal extraction [1]. In fields such as mineral processing or extractive metallurgy the lack of information about minerals surfaces and interfaces has been probably one of the major limitations towards the full understanding of many, and even simple situations, such as how and at which rate a metal sulphide compound, originally present at relatively significant depths in the earth crust, oxidises when it is exposed to atmospheric conditions. As in many human activities, the development of innovative technologies in mining or related fields like mineral processing and/or extractive metallurgy are usually reactive rather than proactive: it is more a challenge-driven journey [2]. Only as a matter of exemplification, in the case of copper beneficiation, two types of processes (**Figure 1**) have been designed and implemented at an industrial scale throughout many decades with relatively relevant, but small variations. The presence of copper oxide minerals in an ore is commonly associated with the implementation of hydrometallurgical paths where leaching operations have proved to be efficient even for low grade ores, known as dump leaching [3, 4]. The presence of copper sulphide minerals, though, is preferentially linked to the pyrometallurgical line of process, where froth flotation operations have shown to be especially successful in selectively separating the economically valuable minerals, particularly nowadays when the copper grade at many mine-sites experience a steady decline [5]. It is important to highlight that this apparently direct correspondence between mineralogy and the associated commercial process has evolved to some extent in the last few decades, at least scientifically-wise. Enormous efforts have been made by major mining companies and research institutions to move forward towards developing new technologies to deal with sulphide minerals via hydrometallurgical processes. Examples of this include the leaching of concentrates,

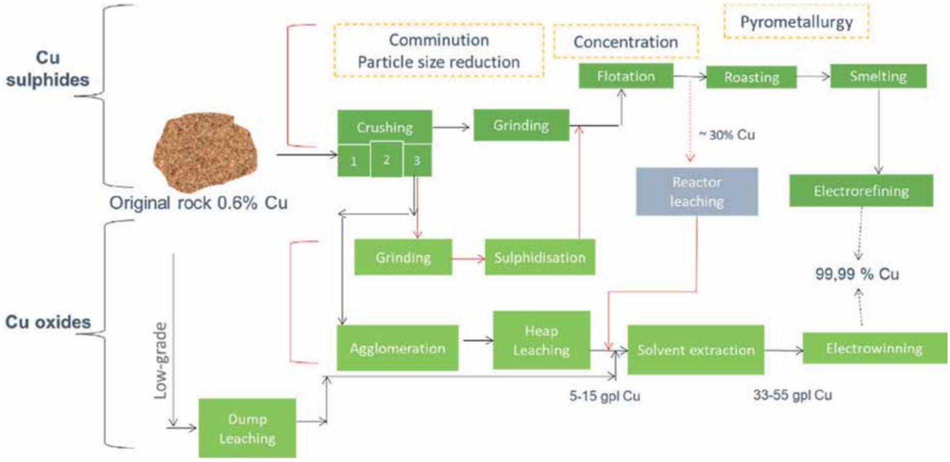

Figure 1.
Block diagram of the major paths of copper beneficiation. Note: Cu sulphides show the path (upper part of the scheme) of comminution-flotation-pyrometallurgical operations and electrorefining, while Cu-oxides show the path (lower part of the scheme) of crushing-agglomeration-leaching-solvent extraction and electrowinning. The scheme also shows how these two lines of process may be connected. For instance, oxides may be milled, sulphidised and follow the Cu-sulphide path; or sulphide concentrates may be leached and follow the Cu-oxide path.

leaching of primary copper sulphide bearing ores using different strategies such as bioleaching, galvanic assisted leaching processes, leaching using seawater, etc. [4]. On the pyrometallurgical path, however, the development has not been necessarily focused on developing the froth flotation of metal oxides, mainly due to difficulties associated with the reagents selectivity, which may be overcome by implementing operations such as sulphidisation of metal oxides [6]. Instead, a large amount of research has been put in place to improve the efficiency of froth flotation operations so as to turn them more sustainable, tackling classic issues such as fines and coarse particles flotation, and other not that classic such as increasing the efficiency of large flotation cells, among others [7, 8].

In the following sections, a few challenges related to mineral processing and extractive metallurgy of copper are presented. This section does not intend to provide a comprehensive list of unsolved situations that metallurgists and professionals working in related fields of knowledge are attempting to resolve. Alternatively, two case studies are presented only to provide a background for a simple and common understanding of some of the difficulties encountered when tackling specific issues mining companies and research centres across the globe face daily, naturally emphasising the role of surface chemistry of minerals in them.

1.1 Challenge in hydrometallurgy: The leaching of primary sulphide minerals

The success of a leaching (or dissolution) process of economically valuable elements from a specific ore strongly depends on the chemical nature of the minerals present bearing these elements and the crystal structure in which these elements are present. In fact, based on the previously mentioned information, feasible leaching agents are commonly screened and selected. Such dissolution has been proved to readily occur in many cases when the valuable element is a metal, and the structure consists of a metal oxide exhibiting basic behaviour [9]. In this case, the reaction between the solid structure and an acid aqueous solution proceeds following a classic neutralisation reaction, which may reach high reaction conversions (close to 80% or higher), under good liberation of minerals to be dissolved and adequate pH conditions of the aqueous phase [10]. Nevertheless, whenever the structure is a metal sulphide, the chemical reactions become complex. For instance, let us examine the classic leaching reaction of chalcopyrite in an acid medium in aerated conditions (Eq. 1) [11–15].

$$CuFeS_{2(s)} + O_{2(g)} + 4H_3O^{+}_{(aq)} \rightarrow Cu^{2+}_{(aq)} + Fe^{2+}_{(aq)} + 2S^{0}_{(s)} + 6H_2O_{(l)} \tag{1}$$

According to Eq. 1, one mol of chalcopyrite should react with one mol of oxygen and four mols of protons, producing one mol of cupric ions and one mol of ferrous ions, which will be kept in dissolved state. Nevertheless, this explanation, in practical terms, is not accurate. The lack of accuracy has nothing to do with whether the reaction is quantitative or not. It has more to do with the fact that chalcopyrite at its surface transforms into something else, even before getting in contact with the aerated aqueous solution. Indeed, whenever mineral sulphide species are exposed to air and moisture, corrosion reactions are triggered. In the reaction of chalcopyrite, only the formation of one mol of sulphur is presented but this is a simplification to explain the inhibition of subsequent copper extraction stages. Therefore, a more detailed description of the process is required, particularly when in the first place, it is not clear whether chalcopyrite, as straightforwardly stated in the reaction, is the actual structure participating in that reaction.

In fact, in this case, it has been indicated that the leaching of chalcopyrite follows a series of steps, the first one being the release of iron (II) ions to the aqueous solution (**Figure 2**). To achieve this, the weakening of iron–sulphur bonds is required leaving a surface structure enriched in sulphide linked to copper atoms, originally described as CuS_2^* and broadly known as polysulphide [18]. The next steps in chalcopyrite oxidation have been associated with the oxidation of intermediate species eventually leading to transpassive dissolution mechanisms [19, 20]. Other authors have indicated the formation of more stable species like haematite, chalcocite-like structure, which can then be oxidised to covellite-like structure, and even copper and iron oxide species [20, 21]. Besides all the discrepancies and controversy behind this subject, the somewhat unknown structures formed, in practice and at large scale, say in heap leaching operations, overall lead to the formation of a passivating layer, which, regardless of whether it is elemental sulphur, metal oxides or oxy-hydroxides, sulphates, or jarosite, the layer, exhibits low electric conductivity [22]. Such conditions allow copper extractions close to 10%, which is too low for this process to be implemented on a large scale. New strategies to leach ore bearing copper primary sulphide minerals such as chalcopyrite are then required.

Indeed, both solubility and electrochemical reaction mechanisms are then inhibited. These findings provide a good indication that for an electrochemical reaction to

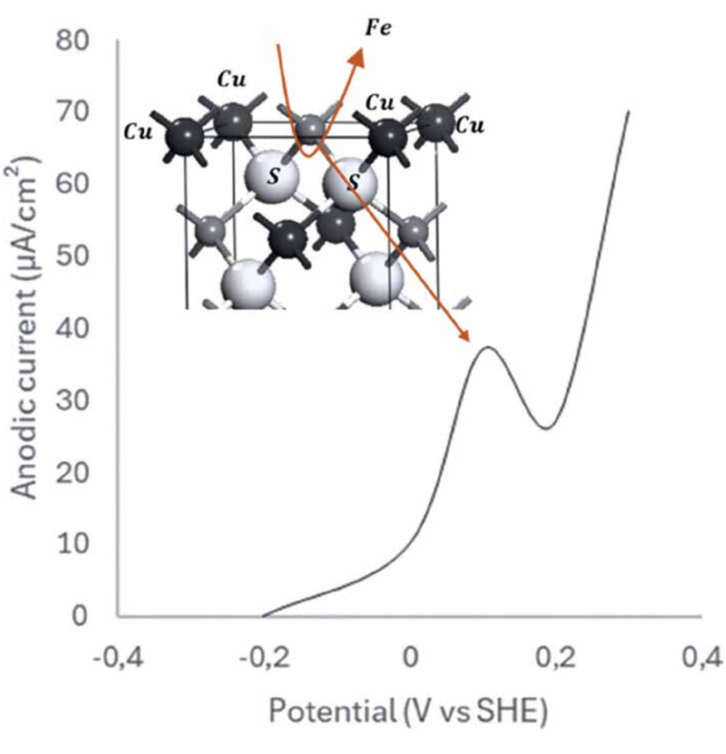

Figure 2.
Sketch of current density (I) vs. voltage (E) graph for the progressive chalcopyrite oxidation of a massive sample mounted in epoxy resin, which entails a first step where iron is removed from the surface structure leaving a Cu-depleted sulphide surface (modified from [16, 17]).

proceed not only the presence of oxidant and reducing agents are required, but also a compound or element acting as an electron/ion carrier (in some cases the reacting agents facilitate the charge transfer, but that is not always the case).

Some of these new strategies, like bioleaching, leaching assisted by galvanic effects, among others, have claimed to achieve higher copper extractions because of the permeability increase of the sulphur (or any other inhibitor) being formed allowing reactant and reaction products to be transported across leading to higher copper extractions. Notwithstanding these empirical observations, a detailed understanding of how such permeability may be modified changing other parameters, like aqueous phase composition or external forces, has not been fully conceived [23].

1.2 Challenge in mineral processing: Froth flotation of primary sulphide minerals

In mineral processing, froth flotation is probably the most used large-scale operation to selectively separate minerals. Its selectivity relies on a property named "hydrophobicity", which has the peculiarity that it applies to the surface of minerals. From an industrial perspective, it is largely dominated by the adequate selection of chemical reagents [24]. This property, widely reported and analysed by many authors, after more than a 100 years froth flotation history, is still a matter of debate. Some authors have proposed a model where hydrophobicity is provided by a layer of gas adsorbed at the mineral surface, a theory that has been found to be plausible to some extent [25]. However, behind all these unknowns, there are at least three aspects on which authors have reached to a certain agreement:

i. Hydrophobicity. In general terms, organic molecules usually do not exhibit polarity as significant as water molecules [26]. This difference reduces the ability of these species to solubilise in each other; therefore, the adsorption of the organic species onto mineral surfaces may to some extent contribute to repelling water at different levels producing various grades of hydrophobicity [27]. And, indeed, it has been confirmed that the presence of organic molecules adsorbed on the mineral surfaces reduces the surface energy of mineral particles, promoting hydrophobic properties on these surfaces. This property has been commonly described in terms of the contact angle and other measurements [28]. For more detailed information, there are some reviews on the subject [29, 30].

ii. Role of sulphide mineral surfaces. Sulphide minerals are known to appear at greater depths in the earth crust compared to oxide minerals [31]. Therefore, whenever they are exposed to atmospheric conditions close to the earth surface, the presence of oxygen and other factors facilitate, among others, oxidation reaction mechanisms. Oxidation, as previously mentioned, will undertake a number of reaction steps and this process is crucial to establish the required hydrophobisation of mineral surfaces. Specifically, in this case, hydrophobisation is achieved by taking advantage of redox reactions where oxygen is reduced and the reagent promoting hydrophobic properties is absorbed after being oxidised. That is the common case of thiol-type of reagents [32].

Nevertheless, even before dosing organic reagents, copper primary sulphide minerals, as well as many other metal sulphides which are floated at pH values close to 10–11, exhibit the so-called "self-induced flotation" where the production of elemental sulphur should not occur; however, it has been proven otherwise.

One probable mechanism that can explain such behaviour is a decrease in the local pH through a similar approach to the previous example that may be of use. **Figure 3** shows a Pourbaix diagram to better represent this situation. Pourbaix diagrams provide information about the regions of relative (not absolute) predominance of specific chemical species [33] and the most common use of the diagrams involves superimposing different diagrams. According to Garrels (1965), chalcopyrite is a mineral that remains stable across a wide range of pH values [34]. If iron (II) ions are transferred to the aqueous solution, hydrolysis will occur, reducing the pH locally. At the mineral surface a mixed potential will be established between oxygen reduction and further steps of oxidation reactions undertaken by the surface compounds being formed. At that pH condition, the excess of sulphur element present originally as sulphide ions at the mineral surface will be close to the region where elemental sulphur is stable, eventually promoting its production. This could confer certain hydrophobic properties to the mineral surface. However, such hydrophobicity enabling the so-called self-flotation of many sulphide minerals is not strong enough to achieve a high selectivity. Early studies have shown that we can profit from the inherent instability of sulphide minerals in aerated conditions enhanced by the presence of water together with the relatively important electric conductivity sulphide minerals exhibit. In this case, the reduction reaction of dissolved oxygen must be tuned with the oxidation reaction of organic molecules so as to avoid overoxidation which might inevitably lead to the formation of oxide structures inherently hydrophilic or underoxidation, which may inhibit the adsorption of the organic molecules. Indeed, pilot plant studies have

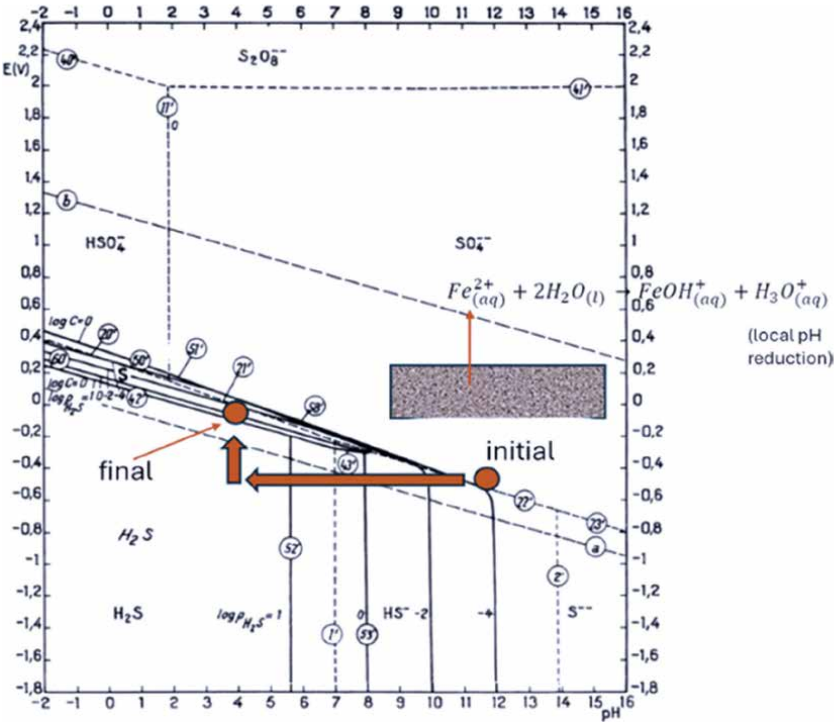

Figure 3.
Sketch of modified Pourbaix diagram enabling the formation of elemental sulphur at the chalcopyrite mineral surfaces even in alkaline conditions where Fe(II) is removed from the surface structure and its hydrolysis leads to a local pH reduction.

confirmed this behaviour. In a project conducted in 2012, three types of ores coming from different mine sites in Chile bearing primary copper sulphide minerals were fed in a pilot plant processing 200 kg/h to a rougher bank that consists of four flotation cells in series (**Figure 4**). Flotation tests were carried out at pH 10.5. The reagents types and doses were implemented according to each site protocol; however, the main collector used was the same: sodium isopropyl xanthate.

Oxygen concentration was tuned in a stirred tank installed before the first cell of the rougher bank. The grinding and classification stages, as well as the stirred tank, were wrapped in plastic and a positive nitrogen gas pressure was implemented to remove most of the air in the system. The oxygen gas concentration varied by injecting air to increase dissolved oxygen concentration or nitrogen to reduce it. The subsequent flotation operation was carried out using air in all conditions. **Figure 5** shows the overall copper recovery results obtained.

As expected, when testing three real ores, only numbered at this time for confidentiality purposes, do not have the exact same response to specific oxygen concentration conditions. The latter can always be explained in terms of the mineralogy of the ore, the water quality or even the transport of reagents, as has recently been reported [35, 36].

1.3 The link between the two challenges: The role of "mediators"

From previous examples, it has been highlighted the relevance of getting proper knowledge of the composition and reactivity of the mineral surface when exposed to a particular fluid. This surface is actually an interface that can be solid–liquid interface or a solid–gas (air) interface, both of which are observed even simultaneously in leaching and froth flotation operations. Since that interface is not necessarily directly connected to the characteristics of the solid bulk phase, it would be difficult to indicate it as the mineral interface. Instead, the common name is "mediator". Mediators, as the word states, mediate between the fluid phase and the solid phase making possible or inhibiting certain physicochemical processes. In metal corrosion during wastewater treatment, this concept has been naturally observed [37]. However, in the case of minerals, the mediator concept has been addressed only by some authors,

Figure 4.
Pictures of the pilot plant used in the project to evaluate the impact of oxygen concentration when dosing the isobutyl xanthate collector (a) oxygen concentration tuning reactor wrapped in plastic, (b) rougher bank.

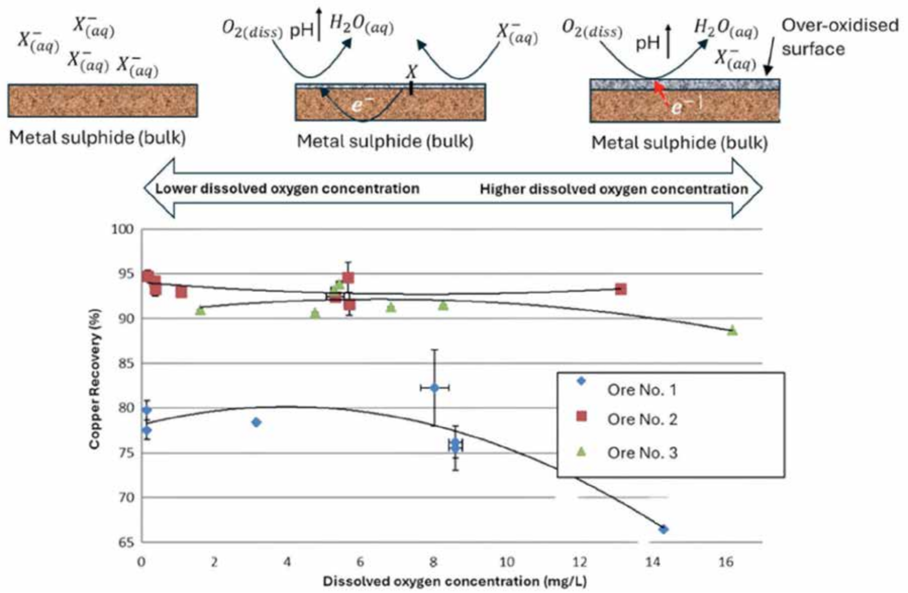

Figure 5.
Impact of pulp conditioning with different dissolved oxygen concentrations ranging from around 0–16 ppm, onto the cumulative copper recovery of three ore types containing primary copper sulphide minerals. The main collector used in every test was sodium isopropyl xanthate at various concentrations (in the figure, represented by X^- *).*

focusing on electron transfer processes [38]. Moving a bit more into details regarding the cases already discussed, the authors present what could be the mediator formed during advanced oxidation of chalcopyrite (**Figure 6**), where Fe(II) ions removal leads to a dissolution-precipitation mechanism, which is later turned into a structure where dissolved oxygen and water build up a structure throughout different elements may diffuse. Having this in mind, the question remains: how do these reactions involving chalcopyrite could be described when oxy-hydroxide species buildup would modify the surface reactivity?. What is the maximum thickness of the oxidation layer

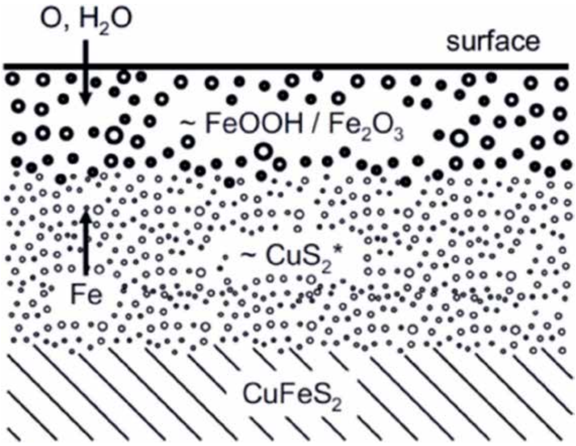

Figure 6.
Model of the interface chemical composition of chalcopyrite when immersed in an aerated aqueous solution at pH 9.2 [39].

formed at the surface of chalcopyrite still making possible to conduct the processes previously mentioned? Or, in the case of the case study related to hydrometallurgy, what is the maximum mediator thickness still allowing copper extraction? How these mediators over time, either formed in acidic or alkaline conditions, may be modified to accomplish good efficiencies? Little information has been published regarding this specific aspect.

Furthermore, even more difficult has been to assess the evolution of that thickness with the residence time of particles in the processes. All the challenges, beyond the specifics behind each process, inherently have a common aspect: the need for a good description of the mineral surface, or more precisely, a correct description of the interface formed between the mineral and a fluid phase, which can be either air or some other gas, or an aqueous phase or some liquid of a different nature.

2. Mediators characterisation: Importance of sample preparation and multi-technique cross-validation

Whenever an industrial process is examined because it is underperforming or for any other reason, sampling protocols are required. Once sampling has been already conducted, the number of sample preparation stages is expected to keep at a minimum to maintain the uncertainty of the results coming from the sample analysis at a minimum [40]. In the case where a sample to be studied is as delicate as the outmost surface layer of a mineral surface is analysed, sampling handling and sample preparation protocols become of high relevance. Studies on how the sample preparation may or may not impact the chemical composition of the outmost surface layer of mineral surfaces are then required or, at least, standardised. By doing so, several case studies may be addressed such as regrinding clean-up of the mineral surface. Ore ageing in pulp phase, over-oxidation due to long residence times in a pulp, optimum surface structures to improve the flocculation when filtering and thickening or other.

Regardless of the selected case study, many techniques have been developed over the last few decades aiming at characterising the outmost surface layer of solid phases, which can, to some extent, be used in studying minerals. Authors have reviewed several surface analysis techniques that have been applied to mineral surfaces with analysis depths of a few nm namely Auger Electron Spectroscopy (AES), Scanning Auger Microscopy (SAM), Low Energy Electron Diffraction (LEED), Reflection High Energy Electron Diffraction (RHEED), Spin Polarised Electron Spectroscopy (SPE), X-ray Photoelectron Spectroscopy (XPS/ESCA), Ultraviolet Photoelectron Spectroscopy (UPS), Secondary Ion Mass Spectrometry (SIMS), Low Energy Ion Scattering Spectrometry (LEIS), Auger Emission Extended X-ray Absorption Fine Structure or (AE)XAFS, Scanning Tunnelling Microscopy (STM) and Glow Discharge Optical Emission Spectroscopy (GDOES) [41].

2.1 Case study on sample preparation: Use of X-ray photoelectron spectroscopy (XPS) analysis

This analytical technique describes the chemical composition and environment observed in solid particles at depths close to 10 nm [42, 43]. This small thickness being assessed under high vacuum conditions (the technique has a working pressure of $10^{-6}-10^{-7}\,Pa$ or below). There is some controversy which indicates that such limit conditions may also change the surface structure and composition. Because of this, other techniques also assessing small thicknesses of a solid phase are recommended to confirm XPS findings. Techniques working at ambient conditions such as external reflection infrared FT technique when dealing with block polished samples or diffuse reflectance infrared FT analysis when dealing with particles samples, are useful [44]. There are several published articles reporting XPS results of mineral samples proving the technique applicability go far beyond froth flotation or comminution in subjects [45].

Relatively recent research studies in froth flotation have been performed incorporating X-ray photoelectron spectroscopy (XPS) during industrial plant surveys. Usually, in froth flotation, the samples coming out of a survey are slurry samples. Therefore, the classic sample preparation consists of a series of steps, which encompasses filtering, drying, splitting into representative samples and the subsequent storing. The whole process, depending on the facilities on site, may take one day as the drying is commonly conducted overnight at a relatively low temperature [46]. This sample preparation process may impact on the results when examining the outmost surface layer of the solid particles compromising the results and the conclusions to be drawn. Leaving aside the potential impact of the drying stage, the relatively high ionic strength process water exhibits due to the water recycling which has been measured and attains values of around 9 mS/cm may contribute to speed up electrochemical reactions or other processes related to slurry ageing. The eventual XPS results could be biased or meaningless.

Considering all the above, an experimental protocol focused on inhibiting further oxidation processes was designed and implemented. Once sampling is performed, the slurry is immediately bubbled with nitrogen reaching a minimum dissolved oxygen of 0.3 mg/L. The filtration is again carried out in anoxic conditions and the solid is washed with distilled water having the same pH as the original sample (**Figure 7**). The pH value is achieved using a known high purity pH modifier, such as sodium hydroxide or other. It must be of high purity to consider this aspect later when interpreting XPS results. Once the filtration stage finalises, a last stage starts where the sample is dried and split into smaller representative samples ready to be submitted to XPS analysis or other (**Figure 8**).

The manner in which the sample protocol was designed is flexible enough to run different tests. For instance, studies on how pH variations due to dosing of specific reagents such as lime, sulphuric acid, or others can be conducted, which can be an opportunity to learn more about these processes.

This sample protocol is not required when the samples are planned to submit to chemical analysis, X-ray diffraction or even Quantitative Evaluation of Minerals by Scanning Electron Microscopy (QEMSCAN) analyses, widely used nowadays to run mass balancing protocols. Considering the QEMSCAN analysis, it is undoubtedly a technique that correlates relatively well with the bulk chemical composition of particles having sizes in the range of those used in froth flotation. The depth of analysis depends not only on the voltage applied but also on the nature of the elements present in the sample. In average, authors have indicated that most of the signal comes from a few micrometres, which at this point could be considered close to that of the solid bulk phase [47]. How do QEMSCAN and other more superficial analysis correlate? This is one aspect to be discussed in the next subsection.

2.2 Case study on multi-technique cross-validation: XPS technique vs. QEMSCAN technique

Just to exemplify the difference in the results coming from two analytical techniques, in a froth flotation process, the three major streams (feed, concentrate and

Figure 7.
Slurry filtering chamber. To remove the air from the chamber, the valves allow injecting nitrogen gas as well as dissolved oxygen-free water towards the end of the filtration stage for washing purposes.

Figure 8.
Oxygen-free glove-box to solids drying and sample splitting under nitrogen gas atmosphere.

tails) were submitted to QEMSCAN and XPS analyses. The XPS analysis was performed using X-ray photoelectron spectrometer - PHI (Physical Electronics) model No. 1257. The sample preparation for the XPS analysis was implemented as in the previous section. QEMSCAN analysis did not require any specific sample preparation. The global relative amount of each element was estimated using the classic sensitivity factors strategy to obtain a semiquantitative analysis of different chemical elements. The latter information was transformed into mass percent by using the atomic masses of the elements involved. And finally, the relative mass percentage resulted from the relative contribution of each of the elements selected to the sum of the relative masses. This last step of computation was applied to element percent from QEMSCAN results. **Figure 9** compares XPS and QEMSCAN results of the three main streams examined.

The feed stream shows the chemical composition obtained with XPS analysis and QEMSCAN analysis. The chemical composition coming primarily from different depths of the sample is, as expected, different. XPS analysis does not report any presence of copper and sulphur, or sodium. These elements are observed in QEMSCAN results, notably the case of sodium where the QEMSCAN results exhibit much higher mass percent. On other side, molybdenum, which appears in small percentages in XPS results, is totally attenuated in QEMSCAN results. The relative iron content percentages obtained with both techniques is somehow similar. The cases of potassium and magnesium show mass percents in the same order of magnitude. Silicon and aluminium exhibit a lower mass percents in QEMSCAN analysis with respect to XPS analysis. Oxygen is predominant in the results provided by both analytical techniques.

In the Tails stream, a similar situation to that of the feed stream is observed with respect to the elements such as copper, sulphur and sodium, which confirms to some extent the consistency of the results associated to the larger mass fractions (feed and tails). In the same way, other elements follow similar trends to those already observed in the feed stream.

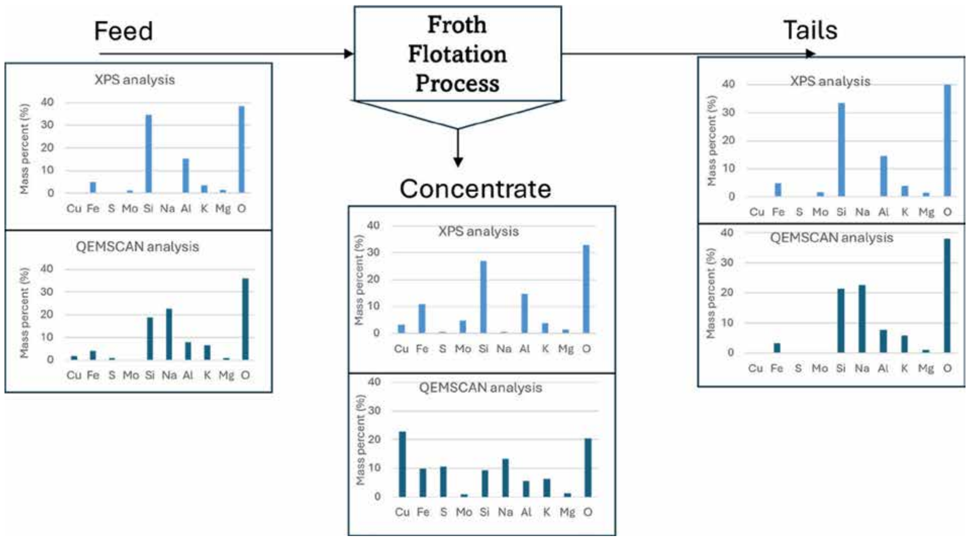

Figure 9.
Comparison between X-ray photoelectron spectroscopy (XPS) and Quantitative Evaluation of Minerals by Scanning Electron Microscopy (QEMSCAN) results for three samples coming from the major streams of a froth flotation pilot plant.

In the concentrate, copper and sulphur signals appear mostly attenuated in the XPS results. Iron mass percents look like the results observed for feed and tails streams. Considering that the major copper-bearing mineral in the process is chalcopyrite the results of iron mass percents are similar regardless of the selected analytical technique chosen which is consistent with all the scientific reports already reviewed that highlight the role of iron as probably the chemical element with higher mass transport in the mediator.

This brief analysis of the XPS results did not even consider splitting the lines into different bands to attempt to identify the proportion of atoms exhibiting different oxidation states, one of the most powerful tools this technique provides.

3. Moving forward: Incorporating aspects of corrosion processes and non-stoichiometry

There are so many challenges when dealing with natural materials, particularly sulphide minerals. Two aspects could be incorporated in the discussion with more emphasis:

3.1 Corrosion phenomena

Whenever a solid surface is exposed to atmospheric conditions, a number of monolayers of water molecules will be adsorbed and vary according to the relative humidity. At 20% relative humidity two monolayers of water have been measured while at 80% relative humidity that number increases up to several tens of monolayers [48]. This effect has an extraordinary influence on the ionic strengths that can be reached when ions are transferred from the solid state to this layer, achieving values close to 10 [49]. More importantly, under these conditions the rate of various processes in the context of atmospheric corrosion can be significant (**Figure 10**).

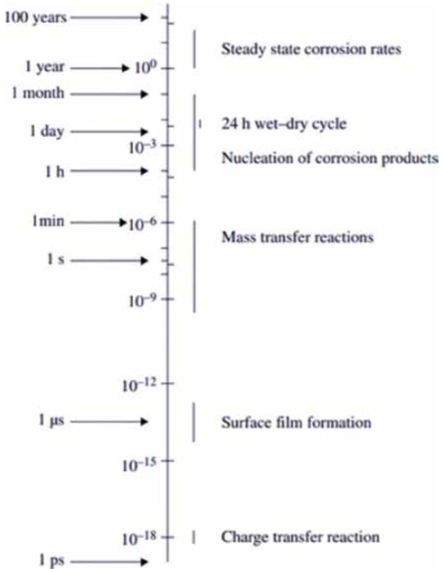

Figure 10.
Rate of some of the most relevant processes observed in solid–gas heterogeneous reactions in atmospheric corrosion [50].

Most of the processes occur in very short periods of time, way smaller than the residence times ores are commonly processed. Moreover, since in mineral processing the fluid phase is often an aqueous phase many of these sub-processes may increase or reduce their rate. The latter can be considered an insurmountable issue or an opportunity. These processes may occur fast but the conditions triggering these processes can be, in many cases, set differently, modifying the processes conditions to avoid some processes to happen or to influence the material to undergo certain reaction paths. Several analytical methods have been applied in the field of corrosion, one of them already mentioned to some detail in this manuscript, such as XPS analysis, but there are more such as infrared, glow discharge optical emission spectroscopy, nanoindentation and nanoscratching techniques, impedance spectroscopy, electrochemical noise technique, scanning Kelvin probe, photoelectrochemical techniques, etc. [51].

3.2 Non-stoichiometry and its link to semiconductor behaviour

Non-stoichiometry is another field of research which has experienced significant advances; however, it has not been widely applied to minerals processing and extractive metallurgy. This topic started at the beginning of the twentieth century, with the study of solid solutions and intermediate phases, which exhibit a range of chemical composition that are characterised in terms of different properties such as melting point, electric conductivity, hardness, etc. [52]. Later, in 1930, the research efforts evolved towards describing crystal lattice defects throughout the Wagner and Schottky model [53, 54].

More recently, authors have connected non-stoichiometry descriptions with the theory of semiconductors, which also looks like that could be a promising link to describe the behaviour of sulphide minerals in mineral processing and extractive metallurgy [55, 56].

4. Conclusions

Many processes, particularly those dealing with metal sulphides, exemplified in the case study of chalcopyrite in this chapter, depends on the chemical composition of unstable surface layers being formed, named “mediator”. To gather information about the mediator structures formed at the outmost surface layer, specific analytical methods are required. Care should be considered with regards to sample preparation protocols when examining delicate information coming from techniques assessing such a delicate volume of control. I was confirmed that the chemical composition procured by two techniques such as QEMSCAN and XPS provide different results.

As some of these techniques aim to capture information coming from the edge of the particles’ surface and examine it under conditions dramatically different from atmospheric, there are chances that the surface may have already changed even before submitting the sample to the analysis. Besides adjusting sample preparation protocols, it would be ideal to crosscheck the information obtained with other analytical techniques to gather consistent data, increasing the chances of reaching a good and unbiased interpretation.

Results coming from changes at the outmost surface of minerals are expected to correlate with complex chemical compositions. Non-stoichiometric analysis may be of use at that point. Linking such valuable information coupled with analytical methods used to assess corrosion phenomena could be a good strategy to move forward in understanding the behaviour of different minerals.

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Chapter 2

Mineralogy in Flotation: Bridging Characterization and Metallurgical Performance

Catalina Martínez-Barrueto and Ignacio Zamora Vega

Abstract

The increasing complexity of copper mineral deposits, characterized by lower grades and growing heterogeneity, demands a deeper understanding of metallurgical processes. In this context, mineralogy emerges as a fundamental discipline to optimize mining operations and maximize valuable minerals recovery. This research analyses the impact of feed mineralogy on metallurgical indicators from the rougher stage in a pilot-scale flotation. Seven ROM (run-of-mine) samples representing different sectors of a Chilean world-class copper porphyry deposit were chemically and mineralogically characterized by atomic absorption spectrophotometry (AAS) and TESCAN integrated mineral analyzer (TIMA)/X-ray diffraction (XRD), respectively. The samples were also tested in laboratory-scale and pilot plant flotation, showing different behaviors according to their original mineralogical features. Multivariate analyses were executed, using correlograms of TIMA/XRD data versus metallurgical results. The results show that the sample's mineralogical variability directly affects metallurgical indicators, proving the relevance of mineralogy in the process optimization.

Keywords: mineralogy, copper, froth flotation, metallurgical indicators, multivariable analysis, porphyry deposits

1. Introduction

The global copper industry faces an escalating challenge: extracting valuable metals from increasingly complex ore bodies. These deposits are often characterized by declining ore grades, heightened mineralogical heterogeneity, and intricate textural associations, significantly impacting the efficiency of traditional metallurgical processes. Consequently, a comprehensive understanding of the interplay between ore mineralogy and metallurgical performance is crucial for optimizing mining operations and maximizing copper recovery. This research delves into this critical relationship by investigating the impact of run-of-mine (ROM) mineralogical variability on the rougher flotation stage. Utilizing seven distinct ROM samples from a Chilean world-class porphyry copper deposit, this study employs a multi-faceted approach, combining detailed chemical and mineralogical characterization with pilot-scale flotation tests. By leveraging advanced analytical techniques, including automated mineralogy

(TIMA/XRD), coupled with multivariate statistical analysis, we aim to demonstrate the direct influence of mineralogical attributes on key metallurgical indicators. Ultimately, this work seeks to underscore the fundamental role of mineralogy in driving process optimization and enhancing copper recovery from complex ore deposits.

1.1 Mining and mineral separation

Mining plays an essential role in modern society, providing indispensable raw materials for infrastructure, energy, and technological development. Copper is a critical component in electrical systems, renewable energy technologies, and electronic devices. The global demand for copper has been steadily increasing: the International Energy Agency (IEA) projects that global copper demand will increase by 50% by 2040 compared to 2023 levels under the Net Zero Emissions by 2050 Scenario. This growth is primarily driven by copper's essential role in electrification and renewable energy technologies. Chile, as the world's leading copper producer, plays a crucial role in meeting this demand, with large-scale porphyry deposits supplying a significant portion of the global market.

However, as ore deposits become progressively complex—lower copper grades and higher mineralogical heterogeneity—efficient mineral processing becomes critical to maintaining economic viability. Various separation technologies are employed in mineral beneficiation, including gravity separation, magnetic separation, froth flotation, and leaching. Among these, froth flotation is the most widely used method for the concentration of copper sulfide minerals, such as chalcopyrite, due to its selectivity and efficiency. This process exploits the differences in surface properties between valuable minerals and gangue, allowing selective attachment to air bubbles and subsequent recovery. Given the growing heterogeneity of copper deposits, understanding the interplay between mineralogy and flotation performance is essential for optimizing recovery rates and metallurgical efficiency. In large-scale mining operations, this knowledge becomes even more necessary to ensure sustainable and cost-effective production in the face of increasing global demand.

1.2 Froth flotation and its element separation efficiency

Froth flotation traces its origins to nineteenth-century discoveries on the separation and concentration of valuable minerals from ores. It is widely regarded as one of the most significant technological advancements of the twentieth century, playing a significant role in the expansion of the raw materials industry [1]. Early research into the mechanisms governing flotation, dating back to the 1930s, focused on wetting and de-wetting dynamics, as well as the behavior of free and wetting liquid films. The process operates by selectively attaching hydrophobic mineral particles to air bubbles, allowing them to rise to the surface and be collected as froth. The fundamental interactions governing flotation involve bubble-particle collision, attachment, and detachment, which collectively determine the efficiency of the separation process [2].

Froth flotation is particularly relevant in the beneficiation of base metals, with copper being the primary focus of this study. Industrial flotation circuits typically consist of grinding and conditioning stages, where reagents such as collectors, frothers, and depressants modify particle surfaces to enhance selectivity. The conditioned pulp is then introduced into flotation cells, where air is injected to generate bubbles that selectively capture valuable minerals. The resulting mineral-rich froth is subsequently collected for further processing, while non-valuable material is discarded as tailings.

The efficiency of copper flotation is commonly assessed using performance indicators such as recovery, grade, enrichment ratio (ER), and mass pull. Recovery quantifies the proportion of valuable mineral retrieved from the feed; grade represents its concentration in the final product. The enrichment ratio (ER) measures the degree of metal concentration from feed to concentrate, while mass pull refers to the percentage of total material (valuable and non-valuable) recovered into the concentrate, serving as an indirect measure of froth stability and flotation selectivity.

Among these, recovery is a core metric, reflecting the proportion of valuable material recovered from the feed to the concentrate. It is classically defined as

$$R = \frac{cC}{fF} = \frac{c}{f} x \frac{(f-t)}{(c-t)} \tag{1}$$

Where:
f: Feed grade (%)
c: Concentrate grade (%)
F: Feed mass flow
C: Concentrate mass flow
t: Tail grade (%)

This expression shows that recovery depends not only on mass distribution across process streams but also on variations in metal content. Expressing recovery in terms of grades underscores the importance of accurately measuring elemental concentrations in each stream. However, it is important to note that flotation separates minerals, not elements [3]. Therefore, recovery based on elemental assays provides only an indirect estimate of separation efficiency.

Since flotation behavior is governed by the surface properties of discrete mineral species, understanding which minerals host the target elements is essential. For instance, copper may occur as chalcopyrite, bornite, or chalcocite—each exhibiting distinct floatability [4]. As such, integrating quantitative mineralogical data is critical for capturing circuit behavior and optimizing performance beyond traditional grade-recovery relationships.

To ensure data accuracy, mass balance calculations and data reconciliation techniques are applied to correct inconsistencies in reported feed, concentrate, and tailings assays. Additionally, flotation kinetics, expressed in terms of rate constants, provide insight into the speed of mineral recovery, while factors such as bubble size distribution and froth stability affect overall performance.

The evaluation of flotation circuits initially relied on simplified first-order kinetic models, which assumed a uniform flotation rate for all particles. However, as industrial applications revealed significant variability in flotation behavior, more advanced models were developed to better represent the complex nature of mineral recovery processes. Kelsall [5] introduced a dual-rate kinetic model for flotation, recognizing that mineral particles exhibit distinct fast and slow flotation rate constants, which significantly improved the predictive accuracy of flotation performance models. By differentiating particle populations based on their flotation response, Kelsall's model enabled a more precise optimization of flotation circuits, influencing reagent strategies, residence time distributions, and overall recovery efficiency.

Modern flotation plants integrate real-time sensors, process automation, and machine learning algorithms to optimize key parameters, including reagent dosage, air flow, and cell conditions, thereby enhancing recovery and reducing losses. These advancements contribute to greater process efficiency and sustainability, ensuring improved resource utilization and economic viability.

1.3 Application of mineralogy to froth flotation

Mineralogy, as a scientific discipline, dates to ancient civilizations, where minerals were identified and classified based on their physical properties. The systematic study of minerals began in the 16th and 17th centuries, with Georgius Agricola [6] pioneering the classification of ores and mining techniques. During the 18th and 19th centuries, advancements in crystallography and chemical analysis refined mineral identification, leading to the establishment of modern mineralogy as a structured field.

By the late 19th and early 20th centuries, mineralogical knowledge became increasingly crucial for industrial applications, particularly in ore processing and metallurgy. The emergence of froth flotation in the early twentieth century as a revolutionary method for separating valuable minerals from gangue further underscored the importance of mineralogical analysis. In this context, optical microscopy provided essential insights into mineral structures and textures, supporting the expanding mining industry.

A major transition in applied mineralogy occurred during the mid-1960s, moving beyond optical microscopy to incorporate more advanced techniques such as electron microscopy and X-ray diffraction (XRD). These innovations significantly enhanced mineral characterization in mineral processing, allowing for more accurate determination of mineralogical properties than was previously possible. As a result, applied mineralogy became an integral tool in ore processing, and many mining operations adopted it as a standard practice.

During the 1960s and 1970s, applied mineralogy was still in its formative stages as a recognized field. However, in the following decade, researchers actively sought to refine mineralogical analysis techniques. Notably, in France, the electron microprobe was developed, marking the beginning of a series of instrumental advancements for mineral characterization. A particularly promising development was the image analyzer, introduced in 1972, which was later integrated with microprobes, energy-dispersive spectroscopy (EDS) analyzers, and specialized software. The high-resolution data obtained from these instruments emphasized challenges in measuring mineral liberation in polished sections, presenting an ongoing research problem [7].

Today, mineralogical analysis plays a fundamental role in optimizing flotation performance. Modern flotation plants rely on high-resolution mineralogical data to improve both recovery and selectivity. Technological advancements now enable automated image analysis, replacing many of the manual processes traditionally performed using optical microscopy. Instruments such as TIMA (Tescan Integrated Mineral Analyzer) and QEMSCAN (Quantitative Evaluation of Materials by Scanning Electron Microscopy) allow for detailed analysis of ore samples and flotation products at the mineralogical level. Since many ore bodies are highly complex, manual microscopy alone is often insufficient for quantitative mineralogical assessment [8]. These advanced techniques enable precise identification of microtextures and provide quantitative mineralogical data, which are essential for optimizing ore processing and flotation performance [9]. The integration of these technologies has transformed flotation from an empirical process into a data-driven, scientifically grounded operation.

The influence of mineralogical texture, including mineral associations and grain size distribution, has also gained prominence in recent decades. It is now widely accepted that mineral liberation and exposure to flotation reagents are critical factors in achieving high recovery and grade. Complementary to automated microscopy, X-ray diffraction (XRD) is essential for identifying hydrated minerals, polymorphs, and clay species that cannot be detected using TIMA or QEMSCAN. Recognizing these mineralogical factors enables operators to mitigate their adverse effects on flotation performance by making process adjustments, such as modifying pH levels or adding selective depressants.

William Petruk, in his book *Applied Mineralogy in the Mining Industry*, emphasizes the growing necessity for specialized expertise in mineralogy, stating that

> *"A dedicated mineralogist is essential at most large mining operations; a person who performs applied mineralogy as an adjunct to other duties can no longer develop the breadth of knowledge and experience that is required to recognize and determine mineral properties that affect different processes. It is also recognized that, to be able to assess what to look for, the applied mineralogist should be a member of a team performing investigations."*

Furthermore, the integration of machine learning and data analytics with flotation systems has further enhanced the role of mineralogy in flotation optimization. By incorporating mineralogical data into predictive models, engineers and researchers can anticipate flotation behavior under different conditions, making these methods particularly valuable for processing complex or low-grade ores with variable mineralogy.

1.4 Scope of the study

This study aims to bridge the gap between mineralogical characterization and metallurgical performance by evaluating the impact of mineralogical variability on copper recovery and mass pull. By integrating mineralogical insights with process outcomes, this study enhances the understanding of how mineralogy controls flotation efficiency, ultimately contributing to the optimization of flotation circuits and process predictability. However, despite advances in analytical techniques such as XRD and TIMA, challenges remain in accurately quantifying complex mineral composition and liberation and linking mineralogical parameters to metallurgical responses with high precision.

2. Mineral characterization

Seven ROM samples were characterized, including atomic absorption chemical analyses for Cu, Fe, and Mo (**Table 1**); automated mineralogical analyses TIMA (**Tables 2** and **3**); and XRD powder and clay analyses (**Table 4**).

The highest copper contents are observed in samples M1 and M4 (0.64 and 0.63%, respectively); M3 has the lowest Cu grade (0.49%). Also, M1 shows the highest Fe grade (4.70%). Mo concentrations range from 30 ppm (M4) to 210 ppm (M6).

TIMA analysis reveals that, on average, the three most abundant minerals are quartz (45.99%), muscovite/illite (27.19%), and plagioclase (9.18%) (**Table 2**). M1, M2, M4, and M7 have similar compositions, while M5 and M6 show slight differences. M5 contains the highest levels of chlorite, and M6 exhibits significant amounts of clay minerals. Both samples also show a notable presence of pyrite. The predominant ore mineral in all samples is chalcopyrite, with an average content of 1.52%.

Sample	Cu (%)	Fe (%)	Mo (ppm)
M1	0.64	4.70	120
M2	0.57	2.30	60
M3	0.49	3.20	105
M4	0.63	1.70	30
M5	0.59	3.80	110
M6	0.55	2.04	210
M7	0.55	2.96	70

Table 1.
Cu, Fe, and Mo chemical results by AAS.

Mineral	M1	M2	M3	M4	M5	M6	M7
Chalcopyrite	1.74	1.63	1.29	1.63	1.62	1.50	1.25
Bornite	0.05	0.00	0.03	0.01	0.01	0.01	0.04
Chalcocite/Digenite	0.03	0.01	0.01	0.00	0.01	0.01	0.01
Covellite	0.00	0.00	0.02	0.00	0.03	0.01	0.01
Pyrite	4.08	1.41	3.82	1.39	5.30	6.74	4.88
Enargite/Tennantite	0.01	0.01	0.00	0.00	0.01	0.00	0.10
Quartz	37.73	46.11	47.48	49.01	43.76	51.96	44.85
K-Feldspar	0.62	9.59	0.04	1.45	0.01	0.02	6.57
Plagioclase	15.78	13.33	0.18	24.94	2.83	0.04	9.17
Biotite/Phlogopite	5.19	0.37	0.58	0.42	0.82	0.01	0.37
Chlorite	7.01	3.07	5.84	2.24	8.77	0.03	3.49
Muscovite/Illite	24.41	21.71	37.04	17.47	32.17	31.45	27.10
Al Clays	2.57	1.56	1.83	0.61	3.14	7.78	1.62
Molybdenite	0.02	0.02	0.02	0.00	0.03	0.03	0.02
Hematite/Magnetite	0.21	0.52	1.16	0.32	0.27	0.08	0.09
Others	0.56	0.68	0.64	0.50	1.22	0.34	0.43

Table 2.
TIMA modal mineralogy results.

TIMA chalcopyrite liberation is shown in **Table 3**. Chalcopyrite is generally ≥80% free, except in M5.

Table 4 presents the XRD results for clay mineral content across the samples. Illite is the dominant clay mineral in most samples, with the highest concentrations observed in M6 (5.44%) and M2 (4.97%). Chlorite also appears significantly in M1 and M3, while kaolinite is most abundant in M3. The total fraction of clays (<2 μm) ranges from 0.50% (M4) to 7.51% (M3), showing notable variation in the clay content across the samples.

Cpy liberation	M1	M2	M3	M4	M5	M6	M7
Locked (<20%)	1.80	0.70	1.00	0.50	2.10	1.20	0.63
Mid-locked (≥20% y < 80%)	17.10	8.20	17.90	9.40	23.50	17.60	8.99
Free (≥80%)	81.00	91.10	81.00	90.00	74.40	81.30	90.38

Table 3.
TIMA chalcopyrite liberation results.

Clay (%)	M1	M2	M3	M4	M5	M6	M7
Kaolinite	0.49	0.26	1.02	0.01	0.25	0.89	0.04
Chlorite	2.29	0.76	1.57	0.04	0.54	0.00	0.24
Smectite	0.07	0.06	0.04	0.00	0.03	0.00	0.00
Illite	4.51	4.97	4.88	0.45	2.18	5.44	1.39
Pyrophyllite	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total < 2 μm fraction	*7.36*	*6.05*	*7.51*	*0.50*	*3.00*	*6.33*	*1.67*

Table 4.
XRD clays results.

3. Experimental procedure

The seven ROM samples were processed in a pilot flotation plant (rougher stage). The tests were executed under identical operational conditions, with the same P80, Cp, reagents, and pH for all samples.

4. Rougher stage results

Samples were collected from the feed, concentrate, and tailings streams of the seven original ROM samples that were processed in the rougher stage. Collected samples were sent for chemical analysis by AAS. A metallurgical balance was performed to determine metallurgical parameters for the rougher stage (**Table 5**).

The results indicate that rougher copper recovery varies between 73.92 and 92.68%. Sample M4 achieved the highest recovery (92.68%), while M5 had the lowest (73.92%). Overall, five out of the seven samples exceeded 80% recovery.

Rougher mass pull ranged from 9.00% (M2) to 21.08% (M3), with samples M3 and M6 exhibiting the highest values. Upon analyzing the mineralogy of these samples, M3 contains the highest levels of muscovite-illite (37.04%), while M6 shows elevated clay content (7.78%) in addition to high muscovite-illite content. The predominance of these species may suggest a higher level of entrainment during flotation, which could affect the concentrate grade [10]. On the other hand, M2 and M7 exhibited lower mass pull, indicating better selectivity in copper separation from gangue minerals.

The rougher enrichment ratio (ER) ranged from 4.04 (M5) to 9.62 (M2). Sample M2 performed the best in terms of selectivity, with a high ER (9.62) and low mass

Sample	Feed Cu grade (%)	Concentrate Cu grade (%)	Tail Cu grade (%)	Cu recovery (%)	Mass pull (%)	Enrichment ratio
M1	0.67	3.89	0.19	75.72	14.02	5.82
M2	0.58	5.21	0.12	81.44	9.00	9.62
M3	0.49	1.88	0.11	81.59	21.08	4.08
M4	0.64	4.44	0.05	92.68	13.27	6.66
M5	0.58	2.65	0.18	73.92	16.17	4.04
M6	0.55	3.01	0.07	89.21	16.37	5.63
M7	0.56	4.34	0.11	83.29	10.78	6.34

Table 5.
Rougher metallurgical parameters of M1–M7.

recovery (9.00%), suggesting a concentrate with a higher copper grade and lower gangue entrainment. In contrast, M5 and M3 had the lowest ER values (4.04 and 4.08, respectively), indicating lower efficiency in copper separation.

5. Multivariate analyses

An analytical approach employing Pearson correlation coefficient correlograms was utilized to evaluate the influence of mineralogical variations on rougher flotation metallurgical parameters.

5.1 Rougher copper recovery

Correlations between rougher Cu recovery and TIMA mineralogy show that chlorite exhibits the strongest negative relationship, indicating that higher chlorite content is associated with lower copper recovery (**Figure 1**). This can be explained by the tendency of this mineral to cause surface issues on sulfide particles, preventing the effective adsorption of collectors such as xanthate. Additionally, chlorite can affect the pulp rheology and reduce the proper dispersion of reagents in flotation [11]. Similarly, biotite/phlogopite and muscovite/illite also show significant negative correlations, possibly linked to slime coating.

The strong positive correlation of quartz with copper recovery suggests that areas rich in this mineral tend to exhibit better metallurgical performance. This may be related to less interference in flotation, as quartz is a gangue mineral that does not consume reagents or affect the hydrophobicity of copper sulfides. Furthermore, the samples show an average of 1.2% of total chalcopyrite associated with quartz, which translates to minimal interference of quartz on chalcopyrite flotation.

Correlations between rougher Cu recovery and clay minerals indicate that all clays are negatively associated with copper recovery (**Figure 2**). Smectite and chlorite show the strongest negative correlations, with values of −0.67 and − 0.64, respectively. Smectite, a highly expansive clay with water retention and reagent adsorption capacity, has been identified in previous studies as a key factor in reducing sulfide recovery due to its effect on pulp viscosity and foam stability. The increase in viscosity reduces the frequency of particle collisions and the mobility of bubble-particle aggregates, resulting in less foam [12]. Chlorite, on the other hand, has been shown to have a

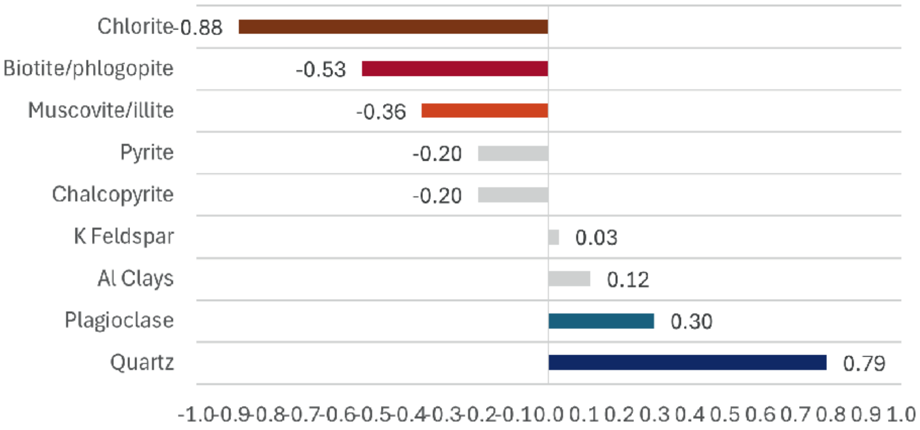

Figure 1.
Rougher Cu recovery vs. TIMA mineralogy correlogram.

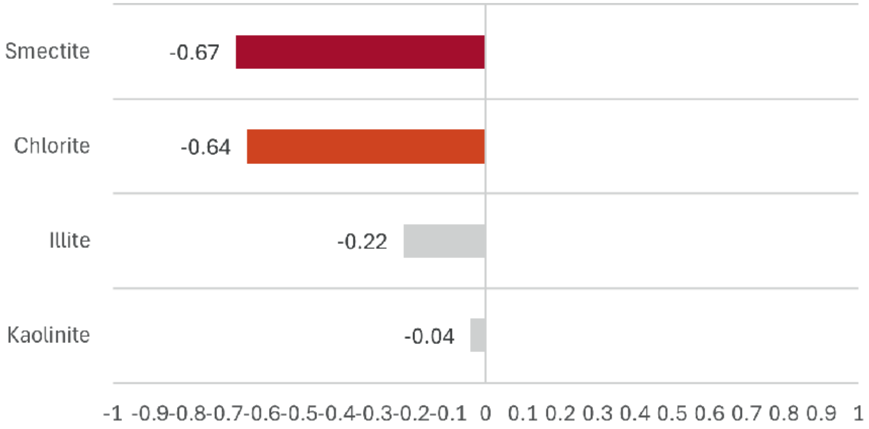

Figure 2.
Rougher Cu recovery vs. clays (XRD) correlogram.

depressing effect on chalcopyrite flotation due to interference with the mineral's surface chemistry, as discussed in the previous analysis. Illite shows a moderate negative correlation of −0.22, indicating a less pronounced impact compared to smectite and chlorite. Finally, kaolinite shows a correlation close to zero (−0.04), suggesting that its impact on flotation is minimal.

Regarding the analysis of Rougher Cu Recovery versus Chalcopyrite Liberation, the highest positive correlation is observed for chalcopyrite with 80–90% free surface (r = 0.61), indicating that a high degree of liberation enhances flotation (**Figure 3**). Particles with a large free surface area provide more exposure for the adsorption of collectors such as xanthate, improving the hydrophobicity and floatability of chalcopyrite. Additionally, the positive correlation for chalcopyrite with 20–40% free surface suggests that even some partially liberated particles can be successfully floated.

Surprisingly, fully liberated chalcopyrite (100%) shows a lower correlation (r = 0.23), as does chalcopyrite with ≥90% liberation. At first glance, this could be attributed to the possibility that fully liberated chalcopyrite mainly consists of very fine particles that cannot be effectively recovered in flotation. However, as will be

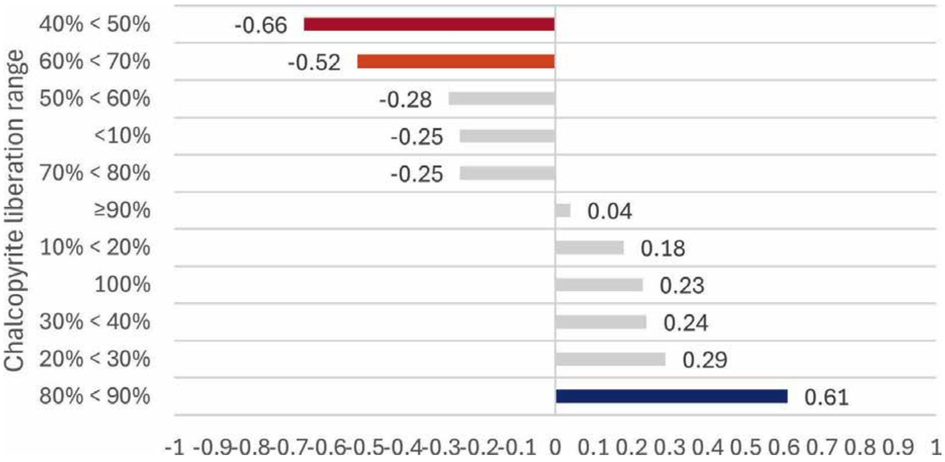

Figure 3.
Rougher Cu recovery vs. TIMA chalcopyrite liberation correlogram.

discussed later, this is not the case, raising questions about the effective representativeness of the mineralogical results.

The 40–50% free surface range exhibits the strongest negative correlation (r = −0.66), indicating that particles in this range struggle to be recovered in rougher flotation. A similar pattern is observed in the 50–70% free surface range, where copper recovery decreases. This behavior suggests that particles with an intermediate degree of liberation may fall into a critical zone where reagent interaction is less effective or where the non-liberated fraction interferes with collector adsorption [13].

5.2 Rougher mass pull

Muscovite/illite stands out as the mineral with the strongest positive correlation to rougher mass pull (r = 0.78), indicating that its abundance is closely linked to higher mass pull. This is consistent with previous studies indicating that phyllosilicates, particularly muscovite, affect pulp rheology and decrease concentrate grade due to entrainment into the froth phase [10].

Pyrite also exhibits a significant positive correlation (0.43), indicating that its presence contributes to greater mass transfer to the froth. Pyrite shares similar floatability properties with chalcopyrite, although chalcopyrite generally floats faster than pyrite in both rougher and cleaner circuits [14]. Other minerals, such as aluminum clays (0.31) and chlorite (0.29), are also associated with higher mass pull (**Figure 4**).

Feldspars show the strongest negative correlations: K-feldspar (−0.83) and plagioclase (−0.60). This suggests that a higher proportion of these silicates reduces mass pull, possibly due to their low hydrophobicity and reduced tendency to be mechanically entrained by the froth.

An interesting result is the negative correlation between chalcopyrite and mass pull (−0.26). Although chalcopyrite is the primary mineral of interest in copper flotation, its inverse relationship with mass pull suggests that a more efficient and selective process could reduce the total amount of floated material without significantly impacting metallurgical recovery. In other words, lower mass pull in flotation may improve process selectivity by reducing gangue entrainment and increasing concentrate grade.

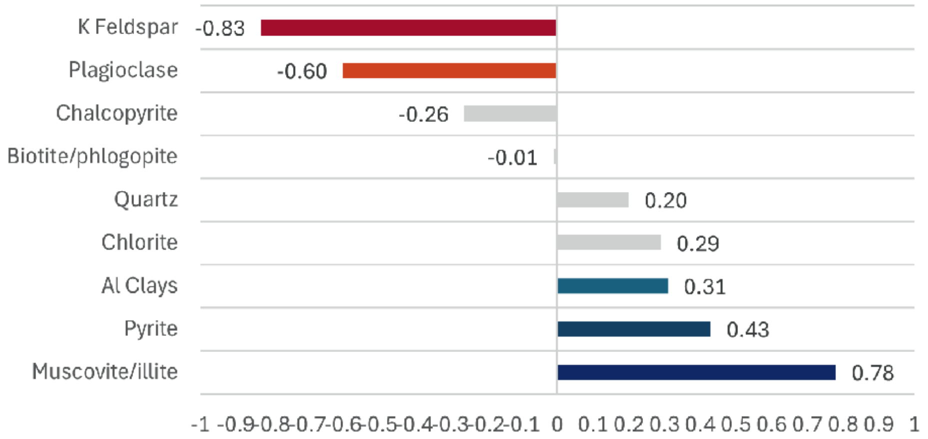

Figure 4.
Rougher mass pull vs. TIMA mineralogy correlogram.

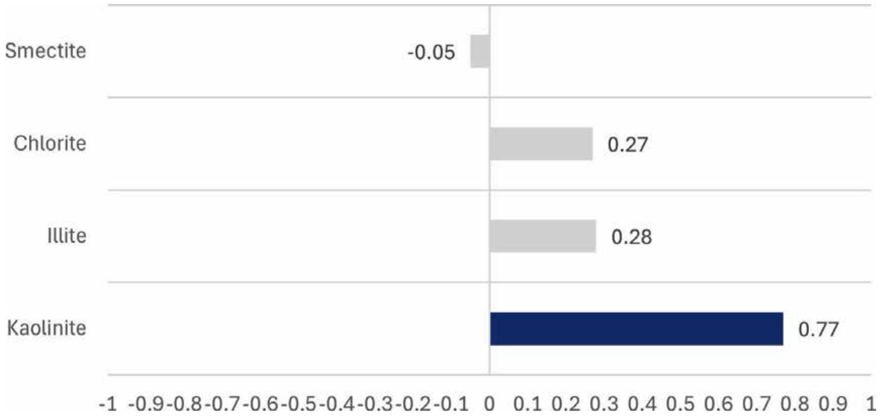

Figure 5.
Rougher mass pull vs. clays (XRD) correlogram.

The analysis results of rougher mass pull versus clays (XRD) show that, in general, all clays have a positive correlation with mass pull. Kaolinite exhibits the highest positive correlation (0.77). This result aligns with previous studies showing that kaolinite, due to its fine grain size and low-density structure, tends to rise into the froth layer, reducing concentrate grade. Additionally, the presence of kaolinite promotes excessive entrainment, characterized by smaller bubble sizes (**Figure 5**) [14].

6. Discussion

6.1 Effect of liberation on rougher Cu recovery

Based on the previously reviewed results, the strong influence of gangue on rougher copper recovery is evident, particularly the impact of phyllosilicates and clays. However, the analysis of chalcopyrite liberation versus rougher recovery is not as conclusive as one might expect. While chalcopyrite with 80–90% liberation shows the highest correlation, it is interesting to note that fully liberated (100%) and fully locked (100%) fractions are not among the most influential variables.

Additionally, samples M6 and M7 achieved high copper recovery values despite having lower chalcopyrite liberation compared to other samples, except for M5 (**Figure 6**). This raises a discussion about the importance of carefully configuring and interpreting data obtained through QEMSCAN/TIMA-type scanning electron microscopy.

It is important to consider that, depending on the laboratory or the mineralogist's criteria, the calculation of mineral liberation can be performed in different ways: it may be based on perimeter (surface area), area, or a combination of both.

If only the perimeter is considered (**Figure 7a**), relevant information about the proportion of the mineral of interest relative to the gangue could be overlooked. On the contrary, if only the area is considered (**Figure 7b**), the actual exposed surface of the mineral in question might be disregarded. This effect is illustrated in **Figure 7**.

Figure 7c illustrates how the calculated liberation value varies depending on whether it is based on perimeter or area. In this example, if chalcopyrite liberation is evaluated based on perimeter, the reported value would be 0%. However, if assessed by area, the liberation would increase to the 40–50% range.

Figure 7d presents another scenario: a quartz grain with a chalcopyrite rim. In this case, perimeter-based liberation of chalcopyrite would be 100%, whereas area-based liberation would not exceed 15%. If a sample predominantly contained "chalcopyrite 100% liberated by perimeter", and automated mineralogical analysis reported liberation uniquely based on this criterion, one might be surprised to find that laboratory flotation results do not align with expectations, potentially yielding a lower-than-expected concentrate grade.

In the same context, the effect of analyzing 3D structures through 2D sections has been deeply studied [15]. This kind of characterization inevitably introduces stereological bias, primarily affecting apparent grain size and apparent liberation [9]. In polished mounts, grains always appear equal to or smaller than their actual size [16]. Similarly, 2D liberation measurements overestimate true 3D liberation, as liberated

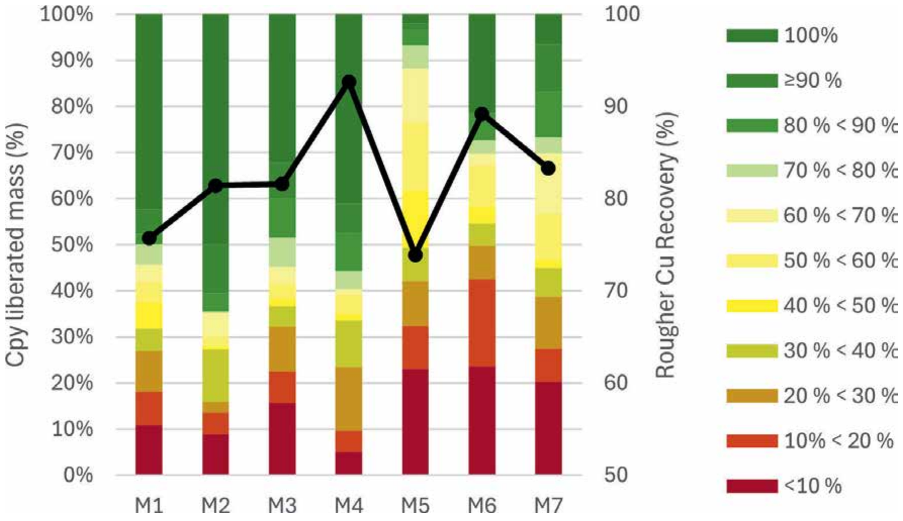

Figure 6.
TIMA chalcopyrite liberation by size and rougher Cu recovery.

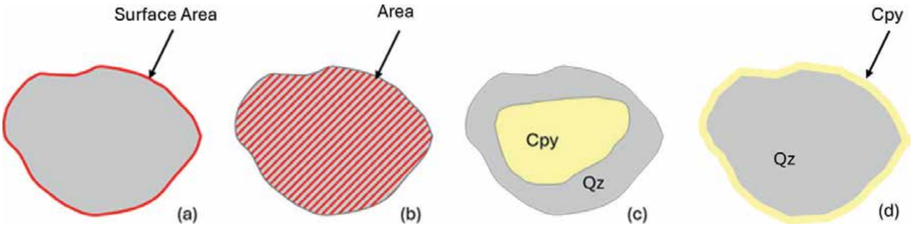

Figure 7.
Liberation criteria in automated mineralogy analysis.

grains always appear liberated in sectional views, whereas locked grains may appear either locked or liberated depending on the cutting plane of the section [17].

The extent of stereological bias depends on particle size, texture, and true liberation state, being more pronounced in simple binary or ternary textures but almost negligible for fully liberated grains. Bias can be mitigated through careful sample preparation, including particle sizing and mounting size fractions in distinct polished mounts [17]. While some authors suggest its impact is minimal in most cases [7], its influence is difficult to quantify, leading to the development of correction methods to account for stereological effects [18].

It is therefore recommended to always confirm with the mineralogy laboratory that the liberation calculation appropriately accounts for these factors, ensuring that the reported data are as representative of reality as possible.

6.2 Importance of chemical reconciliation criteria: QEMSCAN/TIMA

A common expectation is that automated electron microscopy results should align with chemical analyses, with an error margin not exceeding 10–20% for Cu, Fe, and S. However, this expectation implies methodological challenges and may lead to questionable practices in processing mineralogical data.

One of the main issues is the manipulation of data to force alignment with chemical analyses, potentially compromising the reliability of the results. While data preprocessing is essential to eliminate artifacts at mineral boundaries and edges, practices such as particle removal, arbitrary modification of mineral densities, or reclassification of mineral phases can introduce biases in the interpretation of ore mineralogy. Recent studies have highlighted the risks of these approaches, emphasizing that an artificially adjusted correlation between mineralogical and chemical data does not necessarily improve the understanding of a deposit or its metallurgical response.

Another critical factor is the reproducibility of results. Different laboratories may use slightly different approaches for sample preparation, mineral phase segmentation, and the quantification of element-bearing species, leading to variability in reported results. To minimize these discrepancies, it is crucial to establish rigorous methodological standards and foster collaboration between mining companies, laboratories, and research work teams.

Moreover, automated mineralogy still faces limitations in accurately identifying mineralogical species in complex systems, particularly in samples with heterogeneous textures or fine-grained minerals. Advances in mineral classification algorithms, access to more comprehensive mineralogical databases, and the development of systematic correction techniques could enhance the reliability of these analyses.

In this context, ensuring transparency in analytical procedures, cross-validating with complementary techniques, and adopting standardized criteria are key to improving the quality of results. Proper integration of mineralogical and chemical data will enable a more accurate characterization of the ore and more informed decision-making in metallurgical processing.

6.3 Future trends and perspectives

Mineralogical analysis has evolved significantly with the implementation of automated techniques such as QEMSCAN and TIMA, allowing for a more detailed characterization of the minerals present in metallurgical processes, especially when used in conjunction with XRD. However, there are still opportunities for improvement to maximize the utilization of this data and delve deeper into its impact on operational decision-making.

One aspect that can easily be improved is the comprehensive use of the information obtained and reported by mineralogical laboratories. Typically, the review of results focuses on the mineralogical composition, liberation, and association of copper-bearing particles, often overlooking other available information such as the morphology of individual particles, their size distribution, and the theoretical recovery curves. Incorporating a more detailed analysis of the false-color images of the particles could provide a better understanding of their behavior in flotation and other separation processes. Additionally, preparing separate blocks for each size fraction within the same sample would provide more precise insights into the impact of particle size distribution on flotation, always in relation to the granulometric profile of the original material. This approach helps minimize sample preparation biases and ensures that each fraction is appropriately weighted in the final mineralogical result.

Moreover, the integration between mineralogical analysis and metallurgical laboratory data could be improved. Closer collaboration between the departments would enable an easier correlation of mineralogical characteristics with metallurgical parameters, thereby generating predictive models that are more aligned with operational realities.

Looking to the future, it is interesting to consider which innovations could revolutionize mineralogical analysis in mining. Automation must evolve beyond its original purpose and adapt to the new challenges in geosciences. With the growth of geoscience projects, there is a need for a shift toward the use of big data, robust statistics, and machine learning. As an initial broad approach, it is crucial to improve the way in which automated microscopy data is collected and stored [19]. On the other hand, the idea of performing automated mineralogy in 3D using X-ray imaging tools has been a long-standing goal for geoscientists, with recent efforts to make this a reality in the academic sector. Many requirements of automated mineralogy have already been met, such as making quantitative textural assessments of mineral shapes and associations and separating touching particles using machine learning. However, the ability to automatically apply mineral names to the phases identified in the image data remains a challenge [20]. Schulz et al. [19] highlight a breakthrough in this area with μCT, which allows laboratory X-ray instruments to identify mineralogy directly from 3D data without the need for additional chemical analyses. This revolutionizes 3D mineral liberation analysis, which is key to process mineralogy and routine mining studies.

Another valuable integration into mineralogical reporting would be the ability to measure the hydrophobicity of minerals, a fundamental property in flotation. This, combined with the improved mineral characterization obtained through 3D mineralogy, would significantly strengthen the link between mineralogy and metallurgical processes.

7. Conclusions

A comprehensive analysis of mineralogical and flotation data reveals that the composition and textural characteristics of ore significantly impact metallurgical performance. The correlations identified in this study highlight the importance of understanding how different minerals influence copper recovery and mass pull dynamics.

Chlorite, biotite/phlogopite, and muscovite/illite exhibit a strong negative correlation with copper recovery. Among clay species, chlorite and smectite have the greatest influence on copper recovery, both showing a strong negative correlation (chlorite: $r = -0.64$, smectite: $r = -0.67$). Their impact on surface chemistry and pulp rheology leads to increased viscosity, reduced bubble-particle collision frequency, and decreased collector adsorption efficiency.

Quartz shows a positive correlation with copper recovery ($r = 0.52$), indicating that it does not interfere with chalcopyrite flotation. This is likely due to its inert nature, which prevents reagent consumption and hydrophobicity interference.

Chalcopyrite liberation significantly influences flotation response. Particles with 80–90% free surface exhibit the highest positive correlation with copper recovery ($r = 0.61$), whereas those in the 40–50% range display the strongest negative correlation ($r = -0.66$), suggesting a critical threshold where insufficient liberation reduces flotation efficiency.

Muscovite/illite, pyrite, and kaolinite are correlated with increased rougher mass pull ($r = 0.78$, 0.43, and 0.77, respectively), indicating that their presence promotes mass transfer to the froth. This effect can compromise concentrate grade, as muscovite and kaolinite enhance entrainment rather than selective flotation. Kaolinite is the most influential clay in mass pull.

K-feldspar and plagioclase exhibit the strongest negative correlations with mass pull ($r = -0.83$ and -0.60, respectively), likely due to their low floatability and limited mechanical entrainment.

Ore liberation analysis should consider both perimeter and area measurements to minimize biases in flotation performance assessment. Discrepancies between apparent and true liberation suggest that the incorporation of stereological corrections should be evaluated to improve the accuracy of flotation performance assessments. Also, uncritical data manipulation to match chemical analyses may compromise result reliability, underscoring the need for methodological transparency. Integrating mineralogical and chemical data rigorously is essential for enhancing ore characterization and optimizing decision-making in flotation circuit design and process control.

These findings reinforce the necessity of mineralogical characterization for improving flotation efficiency and highlight key factors that influence metallurgical performance. Future work should focus on refining liberation assessment techniques and developing predictive models that better account for textural and compositional variability in flotation systems.

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Chapter 3

Recent Advances in Spectroscopic Techniques for Mineral Characterization

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Abstract

Spectroscopic methods are essential for characterizing minerals because they provide important information about their physical, chemical, and structural characteristics. Recent advances in spectroscopy have significantly increased our ability to investigate complex mineral systems more precisely and effectively. This chapter offers a thorough analysis of the most recent spectroscopic techniques used in mineral characterization, such as advanced electron microscopy, nuclear magnetic resonance (NMR), Raman and infrared spectroscopy, X-ray fluorescence (XRF), and X-ray spectroscopy. Emerging technologies that allow for the real-time analysis of dynamic processes, like *in situ* spectroscopic techniques and synchrotron-based spectroscopy, are highlighted. The importance of these methods in understanding phase transitions, mineral reactivity, and the identification of defects and trace elements is highlighted. The chapter also examines how spectroscopic data and computer techniques can be used to decipher complex mineralogical processes. This chapter presents recent findings and their practical applications, highlighting the transformative potential of advanced spectroscopic techniques in promoting innovation in mineral characterization and related disciplines.

Keywords: spectroscopic techniques, mineral characterization, Raman spectroscopy, XRF, EDS, elemental mapping

1. Introduction

Spectroscopic methods have long been at the forefront of characterizing minerals because they offer important information about their composition, structure, and functionality [1, 2]. Researchers are now able to examine minute characteristics of minerals at the atomic and molecular levels because to the quick development of spectroscopy. These advancements are particularly noteworthy in light of the rapidly expanding global need for minerals, which is being fuelled by the growth of sectors like sophisticated materials, electronics, and renewable energy [3].

Under these circumstances, the ongoing development of spectroscopic techniques presents unmatched chances to further mineral discovery and characterization [4]. Characterizing minerals is essential to comprehending their characteristics, behavior, and uses in a variety of scientific and industrial fields [3]. In mineralogy, spectroscopic techniques have become essential tools because they provide non-destructive, extremely sensitive, and accurate ways to analyze the physical characteristics, structural arrangement, and chemical makeup of minerals [5]. These methods offer important information that supports the identification of minerals, evaluation of quality, and investigation of their industrial uses. The use of spectroscopic techniques has greatly enhanced mineralogical study and its applications by enabling a more profound comprehension of minerals at both the macroscopic and atomic levels [2, 6].

Mineral characterization has advanced even more quickly as a result of the combination of computer tools and spectroscopic techniques [7]. Large datasets produced by spectroscopic investigations are now being analyzed using methods like artificial intelligence and machine learning [8]. The combination of data science with spectroscopy has enhanced the interpretation of spectrum data, enabling more precise forecasts of the characteristics and behaviors of minerals [9]. Furthermore, *in-situ* examinations under field settings are now possible due to the miniaturization of spectroscopic instruments, which cuts down on the time and expense of laboratory-based research [10]. Furthermore, spectroscopic methods have been essential in tackling sustainability issues in mineralogy. Minerals used in environmental applications, such as carbon capture and storage or the clean-up of polluted locations, are increasingly being studied using these techniques. The move to sustainable energy systems depends on the ability to characterize minerals like cobalt and lithium, which are crucial to green technologies. Spectroscopy advances our understanding of these important minerals, which helps us achieve resource and environmental sustainability [9].

Spectroscopic methods have been vital tools for decades, including Fourier-transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) [2, 11]. However, the analytical skills accessible to researchers have been greatly increased by recent developments in these techniques as well as the introduction of new spectroscopic tools including synchrotron-based approaches and Raman spectroscopy [12]. These developments not only enhance the accuracy and precision of mineral characterization, with some techniques achieving elemental detection limits as low as parts per billion (ppb) and spatial resolution improvements down to the nanometre scale, but they also create new opportunities for studying intricate mineral systems that were previously challenging to examine [13]. Recent developments in spectroscopic techniques have transformed the characterization of minerals by improving analytical efficiency and resolution. Technological advancements like Raman spectroscopy, X-ray photoelectron spectroscopy, and laser-induced breakdown spectroscopy (LIBS) have made it possible to map mineral structures, identify trace components, and clarify intricate molecular interactions with previously unattainable precision [13]. Its use at many scales, from nanoscale research to large-scale industrial operations, is one of the most intriguing recent developments in spectroscopic mineral characterization. For example, the characterization of material surfaces with previously unheard-of spatial resolution has been made possible by atomic force microscopy combined with infrared spectroscopy (AFM-IR) [14]. Data interpretation has been further enhanced by the use of automation, artificial intelligence, and machine learning algorithms, which allow for quicker and more precise evaluations of mineral samples [15].

This chapter aims to present a thorough review of current developments in spectroscopic methods for characterizing minerals, highlighting their revolutionary influence on mineralogical study and applications. By examining state-of-the-art techniques and their usefulness, this study seeks to close the gap between basic research and commercial applications, emphasizing the critical function of spectroscopy in mineral science. To demonstrate the scalability and practicality of these methods, special attention is paid to the incorporation of case examples. The chapter demonstrates how advances in spectroscopy transform into useful data, from laboratory-scale inventions to pilot-plant and industrial applications. This strategy shows how adaptable spectroscopic methods are and how they can be used to solve current problems in resource management, environmental sustainability, and mineral processing.

2. Fundamental principles of spectroscopy

The study of how matter and electromagnetic radiation interact is known as spectroscopy. It is an effective analytical instrument for determining the identity of materials and comprehending their characteristics. Molecular spectroscopy can provide information on molecular identity and structure, atomic spectroscopy can only provide information about a sample's atomic or elemental identity [16]. Atomic and molecular spectroscopy include various kinds of transitions: electronic state transitions are usually detected in atomic spectroscopy, although vibrational and rotational transitions can also be examined in molecular spectroscopy [17].

2.1 Interaction of electromagnetic radiation with minerals

In geology, materials science, and mineralogy, the manner in which electromagnetic radiation (EMR) interacts with minerals is a crucial phenomenon [18]. Depending on the mineral's wavelength, energy, and material characteristics, electromagnetic radiation can interact with minerals in a number of ways. EMR reflects off a mineral's surface, a mineral's lustre (such as metallic or vitreous) is influenced by visible light reflection. An example of this reflection includes remote sensing by infrared reflection. The mineral often exciting electrons or causing vibrations in the atomic lattice absorbs EMR energy. Absorption is used to identify visible spectrum color [18]. Infrared absorption provides insights into molecular vibrations and chemical bonding. Transmission occurs when EMR passes through a mineral with minimal attenuation and determines the transparency or opacity of a material [19]. Transmission is applied in spectroscopy techniques such as ultraviolet-visible (UV-Vis), infrared (IR) spectroscopy, etc. Scattering is described as the interactions of EMR with the particles or structure of the material resulting in scattered energy in various directions. Scattering contributes to the appearance of phenomena like opalescence or iridescence. Refractometers measure EMR, which bends to detect minerals when it is exposed to one that has a different refractive index [19]. Electrons in a mineral (such as transition metal impurities like Fe^{2+} or Cr^{3+}) or charge transfer between atoms or ions (such as Fe^{2+}-Fe^{3+} couples) can be excited by electronic transitions in EMR. In spectroscopy, infrared radiation interacts with phonons, or lattice vibrations, to detect functional groups in various modes [20].

2.2 Types of energy-matter interactions: Absorption, emission, and scattering

Absorption, emission, and scattering are important processes in spectroscopy, which studies the interactions of electromagnetic radiation with matter, including minerals. Each of these processes has unique parameters that aid in the interpretation of the interactions. Absorption happens when a mineral absorbs certain wavelengths of radiation, which can excite electrons or cause molecular vibrations [21]. A plot of absorbed light intensity *versus* wavelength or frequency is used to represent the data; Absorbance (A): The logarithm of the ratio of incident to transmitted light is measured using Beer-Lambert Law.

Emission spectroscopy occurs when minerals release energy as photons, usually after being excited by an external source (such as UV, heat, or X-rays). The emission spectrum displays intensity *versus* emission wavelength which can be affected by line broadening and intensity depending on particle size, composition, and incident light wavelength [21]. Line broadening may be caused by Doppler effects; defined as the shift in a wave's frequency with respect to a moving observer in reference to the wave's source affecting. The efficiency with which absorbed photons produce emission is known as the quantum efficiency. Scattering spectroscopy is when electromagnetic radiation interacts with a mineral and is redirected without absorption. Rayleigh scattering includes elastic scattering, where no energy is transferred; important in determining optical properties [21]. Raman scattering, which is a type of inelastic scattering, where energy is exchanged, provides vibrational information about bonds. Brillouin scattering relates to acoustic phonons in minerals. The energy difference between incident and scattered photons is commonly reported in wavenumbers (cm^{-1}) [22], while polarization indicates the orientation of scattered light relative to the incident beam. These characteristics are used to characterize minerals in a variety of spectroscopic techniques, including Raman, fluorescence, IR, and UV-Vis [21].

2.3 Relevance of spectroscopy for structural and compositional analysis

Spectroscopic techniques are essential tools for analyzing the structural and compositional properties of minerals, offering insights into their phase composition, molecular structure, and elemental distribution. Bulk characterization is crucially provided by XRD and XRF, while in-depth molecular and vibrational investigation is possible using Raman and FTIR sensors [3]. Metal oxidation states and electrical structures may be thoroughly studied by sophisticated methods like X-ray absorption spectroscopy (XAS) and Mössbauer spectroscopy [7]. Functions of several spectroscopic techniques for structural and compositional analysis are summarized in **Table 1**.

Spectroscopy provides information about the bonding, vibrational modes, and atomic arrangement in the crystal structure of a mineral [27]. NMR offers information on the coordination and local bonding environment of nuclei such as 29 silicon or 27 aluminum [28]. Analysis of composition aids in the identification and measurement of chemicals, isotopes, and elements in a sample. Inductively coupled plasma optical emission spectroscopy (ICP-OES) is one type of emission spectroscopy that offers elemental analysis that is quantitative [28]. Inductively coupled plasma mass spectrometry (ICP-MS) for trace elements is an example of mass spectrometry coupled with spectroscopy [11]. The technique uses distinct spectra to distinguish between minerals with similar macroscopic characteristics and utilizes shifts or broadening of spectral peaks to identify disorder or defects in crystal structures. The benefit of spectroscopy is its non-destructive nature, many spectroscopy methods maintain the sample's integrity; high sensitivity, by being able to notice minute structural variations and trace components; and lastly, versatility by the ability to analyze gases, liquids, and solids in both normal and harsh environments [28].

Spectroscopic technique	Function	Key features	Common applications	Reference
XRD	Crystal structure determination	High accuracy in phase identification	Mineral phase analysis, crystallinity assessment	[2]
Raman Spectroscopy	Molecular vibration analysis	Non-destructive, high spatial resolution	Identification of mineral polymorphs, structural analysis	[5]
FTIR	Functional group identification	Sensitive to molecular bonding environments	Organic and inorganic mineral characterization	[23]
XRF	Elemental composition analysis	Rapid, non-destructive	Bulk elemental quantification in geological samples	[5, 24]
LIBS	Multi-element analysis	Real-time, *in situ* analysis	Field applications, rapid mineral exploration	[25]
Mössbauer Spectroscopy	Fe oxidation state and coordination	Highly specific to iron-containing minerals	Studies of iron-bearing phases in geological samples	[7]
XAS	Chemical state and local structure analysis	High element specificity	Metal speciation, oxidation state determination	[26]

Table 1.
Functions of various spectroscopic techniques.

3. Overview of advanced spectroscopic techniques

Mineral characterization has been transformed by advanced spectroscopic techniques, which offer remarkably precise insights into the structural, chemical, and electrical aspects of minerals [11]. FTIR and attenuated total reflectance Fourier transform infrared (ATR-FTIR), or infrared spectroscopy are particularly useful methods for detecting molecular vibrations and functional groups in minerals [13]. ATR-FTIR improves surface examination with less sample preparation, while FTIR spectroscopy provides excellent sensitivity and the capacity to analyze a variety of materials [11]. The study of silicates, carbonates, and hydroxyl groups in mineral matrices benefits greatly from the application of these methods. Using inelastic light scattering, Raman spectroscopy is another essential method that excels at providing structural and compositional information [29]. For minerals with complicated lattices, including sulphates and oxides, Raman spectroscopy is a non-destructive and efficient method. Surface-enhanced Raman spectroscopy (SERS) and portable Raman systems are two recent developments that have increased its application to field research and trace-level detection, making it indispensable for forensic analysis and mineral exploration [15, 30]. **Figure 1** displays a schematic diagram illustrating the various sample preparation types and geochemical analysis patterns.

An essential tool for examining the local electronic and structural environment of certain elements within a mineral is XAS, which includes extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) [31]. EXAFS offers comprehensive data on atomic interactions, coordination numbers, and bond lengths, whereas XANES is extremely sensitive to electronic structures and oxidation states. When combined, these methods allow for the characterization of

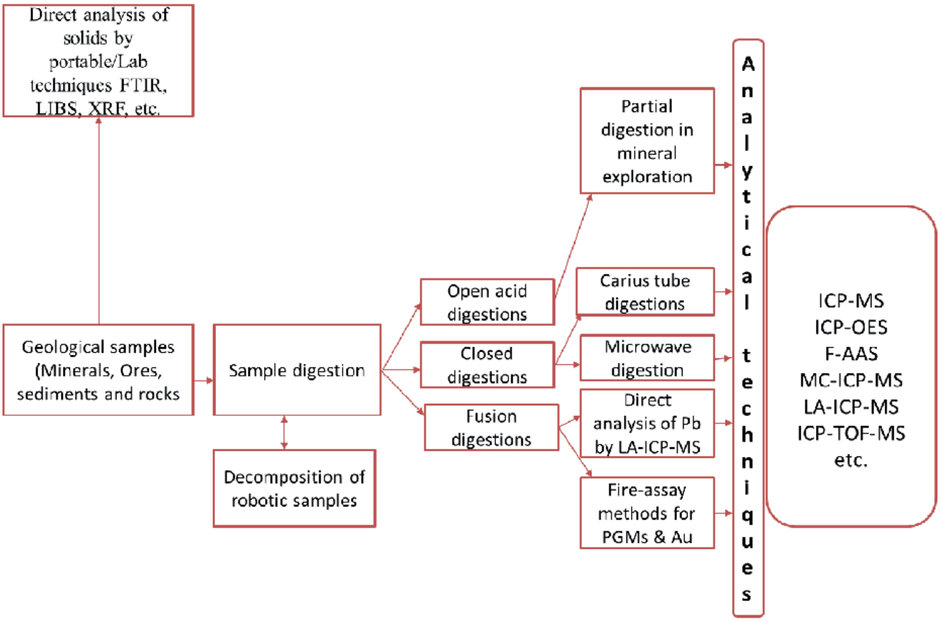

Figure 1.
Schematic illustration of various sample preparation types and geochemical analysis patterns.

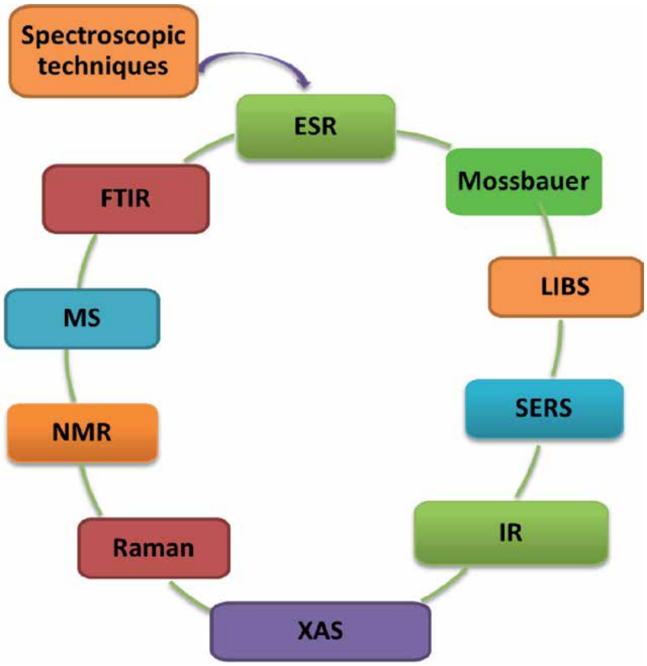

Figure 2.
Various spectroscopic techniques used for mineral characterization.

rare earth elements, transition metals, and other trace elements that are essential to comprehending the genesis and reactivity of minerals [31]. The use of Mössbauer and NMR spectroscopy provides distinct insights into the chemistry of minerals [32]. The local surroundings of nuclei like ^{29}Si, ^{27}Al, and ^{31}P in minerals can be investigated with

Technique	Principle	Strengths	Limitations	Applications	References
Infrared spectroscopy (FTIR, ATR-FTIR)	Absorption of infrared light causing molecular vibrations.	High sensitivity for molecular bonds; ATR-FTIR enables analysis of solids and liquids without extensive preparation.	Limited to surface analysis; challenging with complex mixtures.	Identification of hydroxyl, carbonate, and silicate minerals; molecular structure determination.	[13]
Raman spectroscopy	Scattering of light causing energy shifts due to vibrational modes.	Non-destructive; effective for crystalline materials; complementary to FTIR.	Fluorescence interference; weaker signal for some samples.	Analysis of carbonates, sulphates, and silicates; inclusion studies in gemstones and other minerals.	[15]
XAS	Absorption of X-rays near and above an element's absorption edge, analyzing electronic structure.	Element-specific; effective for local structure analysis; applicable to amorphous and crystalline materials.	Requires synchrotron radiation; expensive and complex.	Oxidation state analysis (XANES); local atomic environment determination (EXAFS).	[26, 31]
NMR spectroscopy	Interaction of nuclear spins with an external magnetic field.	High resolution for molecular environments; applicable to both solids and liquids.	Requires isotopic labelling for some elements; expensive equipment and high operational expertise.	Determination of bonding and atomic structure in minerals such as aluminosilicates and zeolites.	[34]
Mössbauer spectroscopy	Absorption of gamma rays by nuclei in a recoil-free manner.	Sensitive to oxidation state and magnetic properties; element-specific (e.g., Fe, Sn).	Limited to Mössbauer-active isotopes; requires specialized equipment.	Analysis of iron-bearing minerals; characterization of magnetic and oxidation states in ores.	[7]

Table 2.
Comparisons of advanced spectroscopic techniques.

great effectiveness using NMR spectroscopy, which also clarifies structural details in silicates, aluminosilicates, and phosphates. In contrast, Mössbauer spectroscopy concentrates on the magnetic and electrical characteristics of minerals that contain iron. It is crucial for researching iron oxides, sulphides, and other iron-bearing phases because it offers information on oxidation states, site occupancies, and magnetic interactions [32]. **Figure 2** illustrates various spectroscopic techniques used for mineral characterization.

These sophisticated spectroscopy methods help us better understand geochemical processes while also improving the precision of mineral characterization [33]. By facilitating creative applications in mining, environmental science, and materials research, their incorporation into mineralogical studies keeps the discipline moving forward [6]. An organized summary of advanced spectroscopic techniques is given in **Table 2**, which also includes references for additional reading as well as an explanation of their uses, limitations, strengths, and principles.

4. Integration with other characterization techniques

The depth and reliability of mineral and material studies are improved by combining trace element analysis with other characterization techniques. When working with complex systems, in particular, combining complementary techniques enables researchers to obtain a comprehensive understanding of composition, structure, and genesis.

4.1 Complementary use with XRD, SEM, and other methods

The depth and reliability of mineral and material studies are improved by combining trace element analysis with other characterization techniques [35]. Various methods verify one another's findings (for instance, comparing XRF and ICP-MS for trace elements). Combining macro (bulk) and micro (spatially resolved) analyses is known as multiscale analysis. Crystallographic, structural, and morphological data with elemental composition addresses inconsistencies or uncertainties brought on by single-method constraints [36]. Examples of integrated approaches include ICP-MS with XRD to quantify trace elements (ICP-MS) and identify crystalline phases (XRD). The integration ascertains whether trace elements are distributed in the matrix or hosted in particular mineral phases, such as determining the distribution of REEs in monazite or xenotime; XRF with SEM-EDS; XRF for bulk chemical composition; and SEM-EDS for localized elemental analysis. SEM-EDS reveals textural relationships of trace elements identified by XRF [26]. Utilizing integrated methods in ore deposit research shows the separation of trace elements between gangue and ore minerals [26].

4.2 Synergies between spectroscopy and computational modeling

Understanding minerals at the atomic and molecular levels can be achieved through the combination of spectroscopy and computational modeling. The synergy uses spectroscopy to provide experimental data on the dynamics, composition, and structure of minerals and computational modeling to interpret, predict, and explain phenomena that may not be directly observable [36]. The advantages of combining computational modeling and spectroscopy include improved data interpretation.

Computational models identify structural or electronic characteristics of minerals by simulating spectroscopic signals (such as IR, Raman, NMR, and XPS) to match experimental results. For instance, silicate Raman spectra can be modeled to validate experimental peak assignments [37]. Spectroscopic feature prediction, models can detect unknown materials by predicting spectra for hypothetical or unmeasured phases. For instance, figuring out the vibrational spectra of solid phases under high pressure, such as bridgmanite [26]. A better understanding of dynamic processes in computational modeling investigates dynamic phenomena that could affect spectroscopic data, such as phase transitions, chemical reactions, or diffusion. For instance, simulating how temperature affects the IR spectra of carbonates as they break down. While modeling offers input to improve experimental designs, spectroscopy confirms computational predictions [37].

4.3 Multimodal approaches for enhanced accuracy

Complementary analytical methods are combined in multimodal approaches to produce more precise, thorough, and trustworthy results. These techniques combine several data types, including spectroscopic, imaging, chemical, and structural data, to provide a coherent picture of the characteristics and behavior of the material. Multimodal integrates functional, structural, and compositional data for a comprehensive study [38]. Enhanced accuracy in minimizing uncertainty through cross-validation of data across different methodologies. Improved temporal and spatial resolution combines localized chemical or structural information with high-resolution imaging. Micro- and macro-scale feature correlation links microscale phenomena (e.g., grain boundaries) to bulk qualities. Difficulties with multimodal methods include data integration, and complexity; multidisciplinary competence is needed to interpret multimodal data, cost, and time [39]. Applications of multimodal techniques include investigating resources connecting mineralogical phases (XRD) and geochemical anomalies (ICP-MS) to identify ore deposits; monitoring of the environment by combining bonding analysis (XANES) and surface mapping (XRF) to track heavy metal contamination. Material science connects structural features (XRD) and compositional data (EDS) to optimize functional materials [3, 26, 31]. Multimodal models are more accurate since they incorporate various modalities, including text, images, and videos. A more thorough and comprehensive knowledge of the input data can be captured by multimodal AI models, leading to improved performance and precise predictions on a variety of tasks [40].

5. Emerging spectroscopic innovations

Mineral characterization is of utmost importance in various sectors such as the mining industry where time is of the essence. Although there have been advancements in spectroscopic techniques as mentioned in Section 3, the industry requires techniques that have a fast response and turnaround time, which, in turn, improves production. Recently, various techniques that cater to such requirements have been studied and modified to be suitable for mineral characterization. Such techniques include the LIBS, ultrafast time-resolved spectroscopy, and terahertz time-domain spectroscopy (THz-TDS). Furthermore, importance has been placed on coupling spectroscopy techniques with machine learning (ML) and artificial intelligence (AI) in a bid to decrease the time it takes to interpret spectral and statistical data [30].

5.1 Laser-induced breakdown spectroscopy

The LIBS technique is based on the use of laser to create plasma on the sample surface, which causes optical emissions that are specific to specific elements and wavelengths, leading to the production of spectra [25]. LIBS is fast gaining momentum in the mineral characterization industry due to its capability to directly measure a various set of analytes and minerals, including light elements such as lithium, hydrogen, boron, carbon, and fluoride [25]. Furthermore, the laser is able to drill through weathered layers on the sample surface to determine the composition [25, 41]. A further advantage of LIBS is that it can utilized in various conditions (Earth, Mars, and Vacuum) in various states (solid, liquid, gaseous) [42]. Due to its nature of not requiring sample preparation, it minimizes operational costs, therefore, increasing the overall competitiveness of mining companies [41, 42]. LIBS has been applied in the characterization of different matrices such as rare earth elements, lithium ores, and geological ores. A particular study successfully observed and characterized calcium, magnesium, iron, and silicone in basalt and dolomite [42], while other studies quantified lithium in various ores at different grades [25, 43–45]. This further emphasizes the versatility of the technique.

Emerging spectroscopic techniques, such as hyperspectral imaging and synchrotron-based techniques, are transforming mineral characterization by offering rapid, non-destructive, and highly sensitive analysis [46]. Jian et al. [46] used hyperspectral imaging to classify iron ore with water or dust adhesion by combining random forest and differential features. Machine learning classifiers and models with a variety of input features were evaluated for classification accuracy as a means of validation. With respect to the "No dust, no water," "With dust, no water," and "No dust, with water" data, the differential feature considering dust and water (DFDW)-random forest (RF) model obtained optimal accuracies of 87.7, 85.0, and 85.3%, respectively. Their findings could strengthen the applicability of hyperspectral imaging (HIS)-based iron ore sorting and offer technical assistance for its real-world application [46]. Okada et al. [47] optimized multispectral ore sorting with wavelength selection using neighborhood component analysis (NCA) for efficient identification of arsenic minerals. The identification accuracy was similar to hyperspectral data analysis with 204 bands and demonstrated 91.9% or higher when using eight or more bands chosen by NCA. The results indicated that multispectral cameras could be implemented in mineral processing activities in a cost-effective manner [47]. These advancements highlight the growing integration of spectroscopic techniques in both laboratory research and industrial mineral processing.

It is, however, important to note that LIBS does suffer from disadvantages such as spectral interferences due to the heterogeneous nature of most geological ores and rocks. In the characterization of Cr, Ca, and Mg from a complex UG2 Reef ore, the content of the analytes was calculated by factoring in the spectral lines of the analytes that were in close proximity to the targeted analytes, as shown in Eqs. (1) and (2) for Cr, in which I is the intensity of the peak [48].

$$Cr_{\#} = 100 \times \frac{I_{[Cr\,II\,311.86\,nm]}}{I_{[Cr\,II\,311.86\,nm]+} + I_{[Al\,I\,309.28\,nm]}} \tag{1}$$

$$Cr_{\#} = 100 \times \frac{I_{[Cr\,I\,427.48\,nm]}}{I_{[Cr\,I\,427.48\,nm]+} + I_{[Al\,I\,396.15\,nm]}} \tag{2}$$

5.2 Time-resolved and ultrafast spectroscopy

In time-resolved and ultrafast spectroscopy, short pulses of laser are used to study the changes in the properties of various materials on time scales as short as 10^{-16} seconds. This technique is often coupled to other spectroscopy techniques to formulate time-resolved infrared spectroscopy (TRIR), time-resolved fluorescence spectroscopy and time-resolved photoemission spectroscopy [49]. This combination of continuous technological advances with conceptual breakthroughs broadens the application of ultra-fast spectroscopy [50]. Since time-resolved spectroscopy allows for the direct observation of dynamics on timescales that closely match molecular dynamics in real time, it was used for the characterization of titanium dioxide nanoparticles using time-resolved X-ray absorption spectroscopy [51]. In a separate study, time-resolved Raman spectroscopy was used to characterize the mineralogy of a NWA 7533 meteorite [52]. These two studies show the versatility of the technique and the depth it is able to achieve, in terms of characterization.

5.3 Terahertz spectroscopy

Terahertz waves are known waves that are in the range from 0.1 to 10 THz and are situated between the millimeter waves and infrared rays. The terahertz waves have been incorporated into spectroscopy to formulate the terahertz time-domain spectroscopy (THz-TDS) which is often employed to characterize the optical properties of samples including; absorption coefficient, refractive index and phases [53]. THz-TDS is often preferred over techniques such as scanning electron microscopy (SEM), Raman or XRD spectroscopy as it is non-destructive, measures in real-time at a high signal-to-noise ratio, performs at a high speed, offers low ionization damage and has a strong penetration and distinct fingerprinting transformation [53–56]. In this technique, the time-domain signal that is produced is transformed using the Fourier transform to obtain the frequency domain spectrum and subsequently calculate the refractive index ($n(\omega)$) and absorption coefficient ($\alpha(\omega)$) as in Eqs. (3) and (4) [53].

$$n(\omega) = \frac{\varphi(\omega)c}{\omega d} + 1 \tag{3}$$

$$\alpha(\omega) = \frac{2\kappa(\omega)}{c} = \frac{2}{d} ln \frac{4n(\omega)}{A(\omega)(n(\omega)+1)^2}, \tag{4}$$

where A and φ are the amplitude ratio and phase difference between reference and sample signals, ω is angular frequency, c is the speed of light in vacuum, d is the sample thickness and K is the extinction coefficient [53].

Based on the behavior of the absorption coefficient and the refractive index, conclusions can be made regarding the interactions that occur during analysis. For example, in the analysis of a pyrite sample by THz-TDS during pyrolysis, a strong absorption was observed in the spectrum due to the conversion of the ferrosilicates to magnetite [53]. This placed emphasis on the importance of THz-TDS to characterize samples while they are undergoing phase transformation. This capability reduces the time it would take to gather the characterization information with other techniques. Furthermore, THz-TDS can provide important information about the relationship between the creation, genesis, evolution and mineralization of granite, gabbro, and clastic rocks [57, 58], while also having the capability to differentiate mineral phases with varying concentrations, porosities, and masses [54].

6. Applications in mineral characterization

Spectroscopy is essential for characterizing minerals since it can reveal information about their composition, structure, and physical characteristics [2]. The following are some important uses for mineral characterization; mineral identification, structural analysis, elemental and isotopic composition, optical properties, thermomechanical analysis, mining and exploration of resources, among others. Benefits of mineral characterization include high precision, which identifies minute changes in structure or content; non-destructive, the majority of methods keep the mineral sample intact and versatility in that applies for industrial, laboratory, and field environments [59].

6.1 Structural elucidation of minerals at the molecular level

Molecular-level structural elucidation of minerals entails examining their atomic configuration, bonding relationships, and crystal lattice structure [60]. Hattingh et al. [61] investigated the clarification of the molecular and structural characteristics of common South African coals. The researchers found through the use of laser-desorption ionization mass time-of-flight spectroscopy, the molecular weight distributions of the four coals were comparable up to 1800 m/z [61]. Compared to the other three coals, coal TSH exhibited the highest abundance at a higher molecular mass (608 m/z). Understanding the stability, behavior, and characteristics of minerals under various environmental circumstances requires structural elucidation. These assessments employ a variety of sophisticated techniques such as X-ray, XAS, Raman spectroscopy, electron microscope, and LIBS. The periodic arrangement of atoms in a crystal lattice causes X-rays to be diffracted, according to the crystallography principle [62]. Lattice parameters and atomic locations are the main outputs. The principle of XAS is to measure the absorption of X-rays close to an element's absorption edge, yielding information about local atomic environments. Key outputs include bond distances and coordination numbers, as well as the oxidation states of particular elements (e.g., Fe^{2+} vs. Fe^{3+}). Applications include the analysis of environmental minerals for heavy metal sequestration and the study of Fe and Mn behavior in oxides and silicates. The fundamental idea behind NMR spectroscopy is the detection of interactions between atomic nuclei and their electronic surroundings in a magnetic field [59]. Fine details regarding bonding and electrical structures are provided by electron energy-loss spectroscopy (EELS) [59, 63].

6.2 Phase identification and quantification

Determining the types of crystalline (or inevitably amorphous) phases present in a sample and their relative abundances is a crucial step in mineralogical, petrological, and industrial studies. The mineral content and texture of prepared rocks can be reliably determined using quantitative mineral analysis (QMA) employing energy-dispersive x-ray spectrometry and scanning electron microscopes (EDS-SEM) [64].

This data aids in determining a deposit's worth and in streamlining the mining and milling operations. Amayo et al. [65] studied the reversed-phase high-performance liquid chromatography (HPLC) coupled to high-resolution ICP-MS and high-resolution electrospray MS simultaneously without species-specific standards for the identification and quantification of arsenolipids. The decision-making processes that drive the efficiency of mining operations would be substantially improved by real-time analysis of coarse rock streams; however, devices based on electron microscopy are not currently suitable for in-field measurements. Although it has been utilized for elemental analysis in a variety of settings, LIBS has not been used for accurate mineral identification and quantification [65]. Rocks of similar character via spectral matching against an assembled spectral library; and determining sample of geographical origin and provenance are the most popular uses of LIBS in the analysis of geological materials [66].

6.3 Analysis of trace elements and impurities

Understanding the genesis, evolution, and possible uses of minerals depends on the examination of trace elements and impurities. The physical, chemical, and visual characteristics of a mineral can be greatly impacted by trace elements, even in trace amounts. Impurities shed light on the environmental factors and geological processes that led to the genesis of minerals. The origin of a mineral and the circumstances surrounding its formation can be determined by trace components. For instance, zircon's patterns of rare earth elements (REEs) show that it was formed by magma or metamorphism [67]. Hadaad and colleagues, [68] reported a study that introduces a novel LIBS-based approach to mineral identification and quantification that may be expanded to automated mineralogy measurement in coarse rock streams. In order to guide and validate the results that LIBS acquired, a collection of rock tiles from mining activities in Australia was subjected to QMA utilizing an EDS-SEM apparatus. Even when there were mixed mineral phases present in the laser spot area, the identification, measurement, and imaging of minerals on rock tiles were made possible by the use of the multivariate curve resolution – alternating least square (MCR-ALS) approach to the LIBS data [68]. Capannesi et al. [69] reported the INAA's elemental evaluation of contaminants in metallurgical lead samples at trace and ultra-trace levels. A variety of coincidence and anti-coincidence measures were used to characterize materials that were more than 99.99% pure. For the very low element levels, the determination result was quite complicated: the total of Ag, As, Cd, Ni, Sb, Sn, Te, and Zn is less than 100 ppm. High sensitivity and accuracy were achieved at high concentrations by overcoming interferences and matrix effects through the combination of the radiochemical separation process with coincidence and anti-coincidence measurements [69]. Trace elements affect the performance of materials in industrial processes. For instance, quartz's use in electronics may be impacted by aluminum impurities. The value of ore minerals or gemstones is increased by specific trace elements [67]. For instance, traces of gold and silver increase the value of sulphide ores, while chromium gives emeralds their green hue. Understanding impurities is critical for analyzing contamination hazards. While mining, pyrite containing arsenic impurities may pollute the environment. Methods for impurity and trace element analysis include mass spectrometry using ICP-MS. Applications include the quantification of actinides, transition metals, and REEs in minerals by monitoring heavy metal contaminants in the environment [67].

7. Case studies and scale of implementation

7.1 Critical and strategic minerals

The use of sophisticated spectroscopic techniques in industry has transformed *in-situ* mineral monitoring in mining operations. For example, portable FTIR and Raman spectrometers have been used at mining sites to give real-time information about the composition of minerals, enabling prompt decision-making [37]. These methods aid in ore extraction optimization by locating high-value zones and identifying harmful substances that could reduce processing efficiency, including sulphides or clays. This capability is further enhanced by hyperspectral imaging devices that are integrated into mining vehicles or drones, providing spatially resolved mineralogical data across wide areas. These applications have minimized their negative effects on the environment, decreased operating costs, and greatly increased resource utilization. Aoyagi et al. [7] examined the classification of rare-earth minerals enriched in iron-rich deposits using spectroscopic studies of Mössbauer, infrared, and laser-induced luminosity [7]. They used a variety of cutting-edge spectroscopic techniques in conjunction with microscopy to report the specific mineral characterization of RE-containing ores from Yen Phu mine, Vietnam. These techniques included EDS, time-resolved laser-induced fluorescence spectroscopy (TRLFS), infrared microspectroscopy, and Mössbauer spectroscopy. Mössbauer spectroscopic analysis results showed that all three of the ores collected at various places include iron (III) salts other than hematite, magnetite-like, and hematite-like. Additionally, they used infrared microspectroscopic analysis to establish that phosphate was present along the grain boundary in the magnetite-like mineral phase [7].

Due to their demand in various industries, more focus is being placed on the accurate and reliable characterization and quantification of critical minerals using advanced technologies. This includes adapting the quantification of PGMs (platinum group metals) using techniques such as Spark-OES or laser ablation methods that remove the sample preparation step that results in the introduction of errors. With the wide applications of critical metals such as REE and Li in battery materials, major advancement has been made in their characterization, mostly to determine the minerals that they are part of and subsequently, the suitable extraction processes. These advancements include the use of fast and reliable techniques such as LIBS, THz-TDS, XRF, and Raman spectroscopy as shown in **Table 3**. REE ore was analyzed by LIBS in comparison to ICP-MS for La, Nd, Ce, and relative differences between the two techniques were reported as 6.76, 7.09, and 12.95%, respectively [71]. This indicated that either technique can be used, with LIBS having an advantage of ICP-MS due to its lack of sample preparation. One of the industry's predicament is that a critical element such as lithium cannot be quantified accurately using techniques such as XRF or SEM as the fluorescence yield is very low and the matrix can absorb the Li-Kα wavelength. This places emphasis on the widespread use of LIBS as shown in **Table 3**.

In the quest to support the sustainable goal on clean and renewable energy, plenty of research has been carried out on various materials that can store hydrogen [73, 74]. This research and the optimization of such materials are immensely dependent on their accurate and reliable characterization. This is due to that there is need for an understanding of the microstructure, compositional changes and dynamic behavior [73]. Spectroscopic techniques employed are often the XRD, Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS) for the microstructural changes, optical and surface analysis [74].

Year	Mineral	Analyte of interest	Technique	Range (wt. %)	Reference
2022	Li ore	Li	LIBS	0.012–1.3	[25]
2002	Pentalite	Li	LIBS	7.6 ± 1.6	[43]
	Spodumene			6.3 ± 1.3	
	Uranium deposits			2–6.2	
2015	Spodumene	Li	LIBS	2–6	[45]
2019	Doped rock powder	Li	LIBS	0.5–1	[44]
2024	Cerite	La, Ce, Nd	ICP-OES	2–7	[70]
	Xenotime			1–4	
	Monazite			2–6	
	Monazite		ED-XRF	4–10	
2018	Geological ore	La, Ce, Nd	ICP-MS LIBS	0.8–22	[71]
2024	Absolane,	Ni, Co, Mn	Micro Raman	17% Mn 3775 μg/g Ni 2396 μg/g Co	[72]
	Lithiophorite	Li, Mn	Micro Raman	44 μg/g	
2024	Bayan Obo deposit	Oxides of La, Ce, Nd, Pr, Y, Sm, Gd	THz-TDS	0.1–32	[56]

Table 3.
Characterization and quantification of critical minerals using various spectroscopy techniques.

7.2 Environmental and industrial applications

Spectroscopic techniques play a crucial role in environmental monitoring by enabling the precise identification of mineral compositions in contaminated soils and water bodies. These techniques support resource optimization and quality control in industrial settings, guaranteeing effective mineral processing, and material characterization [7]. Olivatto et al. [30] conducted a study on comparison of the primary characterization methods for identifying microplastics in a laboratory experiment including accelerated aging [30]. Their study aimed to assess the effectiveness of SEM with EDX spectrometry, carbon elemental analysis coupled with mass spectrometry, Raman spectroscopy, and FTIR spectroscopy for the characterization of virgin and aged polyethylene and polypropylene microplastics samples. The effectiveness and drawbacks of each method for the thorough chemical characterization of environmental microplastic sample collection are covered in their work [30]. A study was also conducted in Spain focusing on X-ray absorption spectroscopy – XAS, XANES, EXAFS [31]. Catalytic phenomena pertaining to surface, geometric, and electrical aspects were revealed by XAS. Their study showed that in order to better develop more effective and sustainable catalyst systems and processes, XAS can identify structure-activity relationships when used in conjunction with surface-sensitive spectroscopy (Raman, FTIR, ESR) in operando [31]. Pilot-scale research has shown that by offering comprehensive mineralogical information, spectroscopic insights can improve processing efficiency. For instance, Mössbauer spectroscopy has improved magnetic separation methods for iron-rich minerals, while EXAFS and XANES have been used to optimize leaching operations by identifying the speciation of metal ions in ores [7, 31]. Collectively, these case studies demonstrate how spectroscopic methods foster innovation and sustainability in mineral characterization by bridging the gap between scientific research and practical industrial use.

7.2.1 Application of spectroscopy in tailings and waste management

With the drive to reduce ecological footprints, the re-use of mining tailings has seen an increase through the extraction of valuable minerals or setting up the tailings for secondary usage (e.g. brick or glass making). The important part of this procedure is often the characterization of the materials to ensure that the composition is known and processes can be planned around it [75]. Furthermore, in the management of tailings, it is important to ensure that the waste follows environmental regulations, such as the amount of radioactivity that is classified as hazardous as stipulated in the Hazardous Substances Act (15 of 1973), before any disposal of waste occurs. In terms of re-use of tailings for a circular economy, the typical use includes glass and bricks, and use in backfilling. The common techniques used to characterize the material for the mineralogy, quartz, and lime content are XRD, XRF, ICP-OES, and ICP-MS [75–79]. Furthermore, techniques such as SEM and QEMSCAN have been used to determine the phase composition of the tailings to ensure that it is suitable for re-use. In the event that mine tailings are used for backfilling as a form of disposal, it is a requirement to carry out a geochemical assessment and waste classification as per various regulations [80]. This process is important as it involves methods such as the toxicity characteristic leaching procedure (TCLP), in which spectroscopic methods are used to determine the toxicity of the material that is about to be disposed [79].

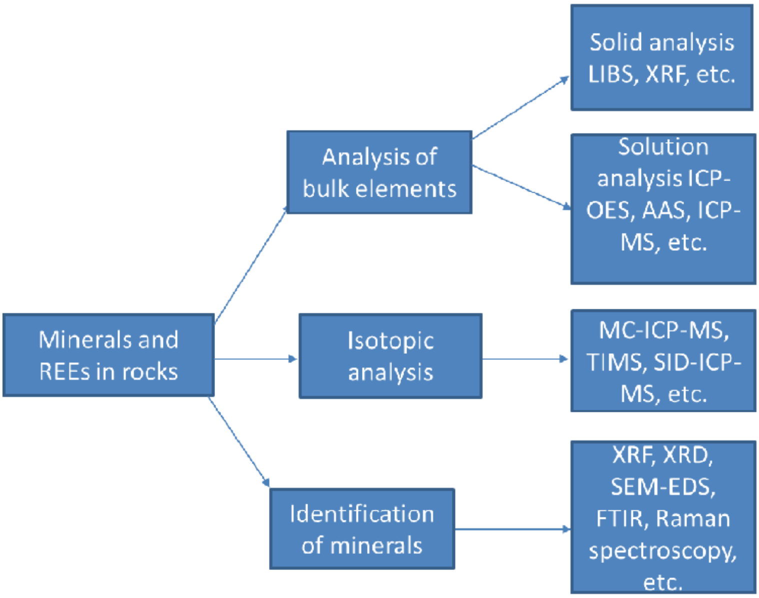

Figure 3.
A schematic illustration of analytical methods utilized in REE investigations.

7.2.2 Monitoring mineral transformations during industrial processing

Reliable monitoring during industrial processing is crucial as it can lead to more efficient plant operations [81]. This typically involves monitoring the intermediate products produced at each stage of the process and it allows for corrections or modifications to be done in order to maximize the process. The monitoring technique to be used often depends on the time it takes the process to move from one stage to another, and those can range from simple techniques such as ICP-OES to complex one such as XRD and FTIR [23]. In a separate study, THz-TDS was used to monitor mineral transformation of pyrolysis products [53]. The several primary analytical methods utilized in REE research pertaining to elemental, isotopic, and mineralogical analyses of geological materials are schematically represented in **Figure 3**.

8. Integration of AI and ML in spectroscopic data interpretation

In the characterization of mineral ores, a handful of data is often produced. This is even more complicated when the data is collected using LIBS, THz-TDS, and other spectroscopy techniques that generate multiple spectral data that need to be carefully deciphered. Furthermore, during industrial processes, fast interpretation of spectral data is required in order for the processes to continue efficiently. This has seen an increase in the incorporation of ML and AI algorithms being trained to handle and interpret spectral data. Algorithms such as Partial least squares regression (PLSR), random forest and multilayer perception (MLP) were used to achieve quantitative determinations of rare earth elements by THz-TDS [55], while in another study, lightweight neural networks were trained to directly predict compound spectra and the probability of chemical bond breakage [82]. In an investigation aiming at the fusing of Raman+LIBS or visible near-infrared radiation (VNIR+LIBS) spectra and the use of ML algorithms to decipher the spectral data, it was concluded that multimethod spectroscopy paired with ML paves the way towards rapid and accurate characterization of rocks and minerals [83].

9. Challenges and limitations

Recent developments in spectroscopic methods for characterizing minerals have the potential to revolutionize the field, but a number of obstacles and restrictions prevent their widespread use. Analyzing complex mineral matrices presents a substantial technical challenge since data interpretation might be complicated by the overlapping spectral signals of many components [84]. For example, it takes extremely specialized knowledge and advanced analytical instruments to differentiate between closely related chemical species or structural characteristics in multiphase minerals or those with amorphous phases [30]. This intricacy may restrict spectroscopy's capacity to offer precise, useful insights in certain situations. Resolution and sensitivity are still major issues, particularly when it comes to identifying trace elements or minute structural differences in minerals [9]. Although highly effective, methods like Raman spectroscopy and X-ray absorption spectroscopy frequently need ideal circumstances, such as pure materials with few contaminants, to produce the required degree of detail [5, 85]. In addition to increasing workload, the requirement for meticulous sample preparation may introduce biases into the analysis, which may not always accurately represent the composition of genuine mineral specimens. In field research

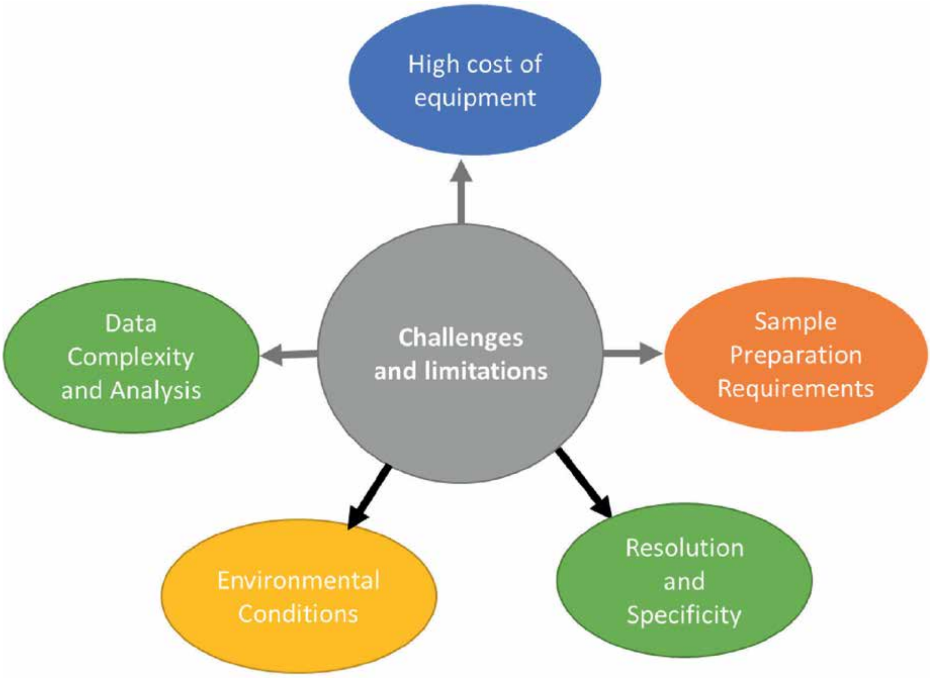

Figure 4.
Challenges and limitations of spectroscopic techniques.

or industrial applications, where sample quality and preparation time are unpredictable or limited, this difficulty is especially noticeable [10]. The high price and limited scalability of sophisticated spectroscopic instruments are two other noteworthy drawbacks [5, 86]. For example, only a few researchers may use synchrotron facilities because of their high cost and limited availability, despite the fact that they offer unmatched analytical capabilities [33, 85]. Because of this, businesses and research teams have major obstacles when attempting to use these methods on a large scale, especially in poor nations [87]. Some of the challenges and limitations of spectroscopic methods for characterizing minerals are depicted in **Figure 4**.

10. Future trends and innovations

The field of mineral characterization is rapidly evolving, with significant advancements in portable and field-deployable spectrometers [1]. These compact and robust devices are designed to provide accurate and real-time data for on-site analysis, eliminating the need to transport samples to laboratories. With improvements in battery technology, sensor miniaturization, and rugged designs, portable spectrometers are becoming indispensable tools for geologists and mining engineers in remote and challenging environments. They facilitate rapid decision-making and reduce operational delays by enabling real-time identification of mineral compositions [88]. These devices also offer non-destructive analysis, preserving sample integrity for further studies. Another cutting-edge development is the growing application of hyperspectral imaging in mineral exploration. Hyperspectral imaging systems capture detailed spectral data across numerous wavelengths, enabling the precise mapping of mineralogical variations over large geographical areas [9]. These systems, coupled with advanced data analytics and machine learning algorithms, allow for the identification of hidden mineral deposits and complex geological features. The integration of drones and satellite platforms with hyperspectral technology has further enhanced its reach and efficiency, enabling extensive and cost-effective exploration [9].

Portable and field-deployable spectrometers have made considerable strides in the fast-changing field of mineral characterization [15]. By providing precise and up-to-date data for on-site analysis, these sturdy and small gadgets do away with the need to ship samples to labs. Geologists and mining engineers in distant and difficult situations are finding that portable spectrometers are essential instruments due to advancements in battery technology, sensor miniaturization, and robust designs [87]. By allowing for the real-time detection of mineral compositions, they speed up decision-making and cut down on operational delays. Additionally, by providing non-destructive analysis, these tools maintain sample integrity for subsequent research [1]. Another innovative advancement is the expanding use of hyperspectral imaging in mineral exploration [8]. Hyperspectral technology's reach and efficiency have been further increased by the integration of drones and satellite platforms, allowing for comprehensive and economical research [8, 89].

11. Conclusions

Spectroscopic methods have become essential for characterizing minerals since they provide a deep understanding of their structure, content, and properties. Recent developments have greatly improved the resolution, accuracy, and utility of these techniques, including hybrid approaches like AFM-IR, synchrotron-based spectroscopy, and Raman imaging. By providing answers for both basic research and real-world applications in fields including advanced materials development, sustainability, and crucial mineral exploration, these advances have closed the gap between nanoscale and industrial-scale studies. Notwithstanding these developments, obstacles including expensive equipment, difficult data interpretation, and the requirement for technique standardization continue to be major obstacles to broad acceptance and efficacy. Future studies should concentrate on creating portable, affordable equipment for field use and enhancing data integration using cutting-edge computational methods like machine learning in order to fully realize the potential of spectroscopic techniques. Additionally, laboratory findings can be converted into workable plans for sustainable mineral discovery and use by integrating spectroscopic techniques into pilot and industrial-scale operations. In addition to improving spectroscopy's place in mineralogy, these initiatives will help satisfy the expanding needs of sectors that depend on strategic and vital minerals.

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Conflicts of interest

The authors declare no conflict of interest.

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Section 2

Environmental Challenges and Sustainability

Chapter 4

Iron Oxide and Hydroxides for the Removal of Heavy Metals from Wastewater

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Abstract

Due to their remarkable adsorptive qualities, low cost, and wide availability, iron oxides and hydroxides have attracted a lot of interest as efficient materials for the removal of heavy metals from wastewater. The mechanisms by which iron-based minerals, such as ferrihydrite, magnetite, haematite and goethite interact with heavy metals through ion exchange, co-precipitation, and adsorption are covered in detail in this chapter. In order to maximise metal uptake efficiency, the importance of surface chemistry, particle size and mineral crystallinity is emphasised. This study critically examines developments in iron oxide functionalisation and modification to improve their capacity and selectivity for particular metals, including cadmium, lead and arsenic. While there are naturally occurring iron oxides/hydroxides, it is possible to synthesise them, coupling the synthesis with surface modifications, and these are usually monitored or verified using easily accessible instruments such as X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM) and Fourier Transform Infrared Spectroscopy (FTIR). This integration of the iron oxides/hydroxides with materials in nanotechnology and polymers has been beneficial for the removal of both heavy metals and other pollutants, such as organic ones, which highlights the versatility of the materials. The ability of the materials to be regenerated for further use makes them attractive in the wastewater treatment industry and in terms of environmental beneficiation. This chapter, therefore, provides a comprehensive analysis of iron oxides and hydroxides, highlighting their crucial role in developing sustainable wastewater treatment systems and reducing heavy metal pollution.

Keywords: iron oxides, heavy metal, adsorption, water treatment, sorption isotherms, wastewater remediation

1. Introduction

Due to the increase in population, the level of industrialisation and agricultural activities has increased exponentially, which indirectly leads to an increase in pollution of the air and (waste) water. The most common wastewater pollutants include heavy metal (HM) cations, hydrocarbons, pesticides, nitrogenous compounds, pharmaceutical residues and phosphorus [1]. Pollutants such as heavy metals, which are characterised by having higher density than water, are of great concern due to their potential to be toxic at low concentrations. Furthermore, HMs are characterised by their high solubility in water, ability to bioaccumulate in living organisms, and their ease of absorption by aquatic organisms, with several studies having detected HM in the gills and muscular tissues of various species of fish [2]. The common or prevalent health impacts associated with HM are brain and kidney damage, are carcinogenic, cause damage to a developing fetus, and damage to the respiratory and cardiovascular systems, making HMs very dangerous (**Table 1**).

The HM of primary concern are reported as arsenic, cadmium, chromium, copper, mercury, manganese, nickel, lead and zinc, with the toxicity ranked as Hg > Cd > Zn > Ni > Pb > Cr [1]. Due to their adverse effects on the ecosystem, several methods have been developed to remove these pollutants from wastewater. Those can

Heavy metal	Health effects	Environmental effect	Sources	Permissible limits
Mercury (Hg)	Carcinogen, brain damage, developing fetus damage	Accumulates in water-laid sediments and converts into methylmercury	Mining, Thermometer and barometer production	0.001 ppm (w) 0.05 ppm (s)
Cadmium (Cd)	Damages to respiratory, cardiovascular and respiratory systems	Bioaccumulates in aquatic organisms and plants	Rock weathering, forest fires, volcanic eruptions	0.003 ppm (w and s)
Lead (Pb)	Memory loss, disturbance of haemoglobin synthesis, kidney damage	Leads to losses in biodiversity, changes community composition and reduces reproductive rates in plants	Batteries, dyes, lead smelting, insecticides	0.01 ppm (w) 0.1 ppm (s)
Chromium (Cr)	Capability to destroy DNA in cells	Negatively affects plant metabolic activities and hampering plant growth and yield	Production of chromic acid, wood preservation, leather tanning	0.05 ppm (w) 0.1 ppm (s)
Nickel (Ni)	Dermatitis, allergies, cancer of the respiratory system	Adsorbs to sediment or soil particles and becomes immobile	Municipal trash international, mining, residual oil burning, fossil burning	0.01 ppm (w) 0.05 ppm (w)
Arsenic (As)	Skin damage, hyperkeratosis, cancer in the skin, lungs, liver and kidneys	Affects photosynthesis and can lead to the inhibitions of growth in plants	Geochemical processes, volcanic eruptions, fossil fuel combustion	0.010 ppm (w)
Zinc (Zn)	Gastroenteritis, peritonitis, growth retardation	When present in soils, it can seep in groundwater	Paints, rubber and chemical industries	5 ppm (w)

Table 1.
Effects, sources and the permissible limits of various heavy metals [2, 3].

be classified into two groups: physical methods (adsorption, ion exchange, membrane technology) and chemical methods (chemical precipitation, precipitation, electrokinetic technology) [4]. While the methods are effective to a certain extent, adsorption is mostly favoured due to the low cost, ease of use and effectiveness [5]. Furthermore, adsorption can be carried out using various materials as adsorbents such as iron oxides/hydroxides, which are easy to make, nanomaterials, plant fibre components and biomaterials.

Iron oxides/hydroxides are one of the most important transitional metals due to their technological use. Various iron oxides/hydroxides are available, which mostly differ in their crystalline structure and their surface area size. These materials are common for HM removal in wastewater as they have high reactivity and photocatalytic properties against wastewater, they possess high surface area, act as a great adsorbent for heavy metals and have a high affinity for diverse functional groups [6]. The iron oxides/hydroxides commonly used for HM removal are magnetite, haematite and goethite, amongst others, with their surface areas being as high as 700 m^2/g (**Table 2**).

Various studies have successfully used and applied iron oxides in heavy metal removal and obtained satisfying efficiencies. Studies have used goethite and haematite for the removal of arsenic through co-precipitation and adsorption, while in China, 67% of removal efficiency was obtained using iron oxides/hydroxides. Furthermore, the ability of these materials to be integrated into other materials such as nanomaterials and graphene oxides make them more attractive, also emphasising their importance and versatility. This versatility of the iron oxide/hydroxides is usually applied in the removal of organic pollutants such as pesticides, dyes and pharmaceuticals. By modifying the materials into iron oxide nanostructures, highest removal efficiencies were obtained for orange dye II, functionalising magnetite with biopolymer resin has led satisfactory removal of methyl orange and acid red 18 from water. Furthermore, ferric oxide nanoparticles have been applied in the removal of wide of pharmaceuticals such as sulfamethoxazole, ciprofloxacin and gemfibrozil.

It is important for a water remediation technique to be environmentally friendly and cost-effective in order to be applied on a larger scale. Adsorption using iron oxides/hydroxides has proven to offer that benefit, in comparison to other traditional methods. This chapter therefore aims at addressing the importance of iron oxides/hydroxides in the removal of heavy metals from wastewater through the use of different mechanisms. Their importance and their capabilities are investigated, together with the extent of their versatility. The use of iron oxides/hydroxides is further emphasised through the formation of hybrid systems, integrating them with

Iron oxide/hydroxide	Chemical formula	Surface area (m^2/g)
Ferrihydrite	$Fe_5HO_8.4H_2O$, $Fe_5(O_4H_3)_3$	100–700
Goethite	α FeOH(OH)	8–200
Akaganeite	β FeOOH	176
Magnetite	Fe_3O_4	4–100
Haematite	α Fe_2O_3	10–100

Table 2.
Types of synthetic and natural iron oxides/hydroxides applied for heavy metal removal in wastewater [7].

nanomaterials, which are very currently broad and have the ability to be upscaled. This chapter further addresses the environmental impacts of these materials, which are particularly minor.

2. Mechanisms of heavy metal removal

2.1 Adsorption processes (chemisorption, physisorption)

There are various mechanisms that are used for the removal of heavy metals from wastewater including chemical precipitation, lime coagulation, ion exchange, reverse osmosis and solvent extraction [8]. These, however, have limitations such as insufficient metal removal, high energy and reagent requirements and they produce waste that requires extensive disposal measures. The alternative is then adsorption due to its simplicity of use, high removal efficiency across broad pH, and low cost. Adsorption is a crucial process in treating municipal wastewater, meeting higher effluent standards and water reuse requirements, and is integral to various environmental processes and operations. The nature of the interactions between adsorbate and adsorbent determines the classification of adsorbent processes, which can be categorised into two mechanisms: physical adsorption (physisorption) and chemical adsorption [8].

The mechanism of adsorption is governed by various models which have the capability to give information on the relationship between the adsorbate and the adsorbent. Although there are multiple models that exist, the frequently used to determine the kinetics are the Langmuir (Eq. (1)) and Freundlich isotherms (Eq. (2)). These models are important in adsorption as they help with interpreting the mechanism of metal adsorption, they shed light on the surface properties of adsorbents and the intermolecular interactions between the adsorbed molecules and the adsorbent matrix [8].

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \tag{1}$$

$$q_e = K_F C_e^{\frac{1}{n}} \tag{2}$$

Where q_e is the adsorbed metal ions per unit mass of adsorbent at equilibrium, C_e is the metal ion concentration in solution at equilibrium, K_L is the Langmuir binding constant, $q_{\max}$ is the maximum amount of metal adsorbed per unit weight of adsorbent, K_F is the Freundlich isotherm constant related to adsorption constant, and n is the constant related to adsorption intensity.

Due to the different properties of the heavy metals and how they respond to environmental factors, they can follow different isotherms while in the same solution or exposed to the same conditions. In the case of the removal of Ni^{2+} and Cd^{2+} from water using magnetite nanoparticles and coated magnetite nanoparticles, it was observed that the Langmuir model fitted most of the metals, whilst the Freundlich model only applied to Cd^{2+}. This was observed in a series of experiments, which included varying pH and the concentration of the adsorbent. The $q_{\max}$ values for nickel were affected by an increase in the adsorbent dose due to the increase in the number of present active sites, however, due to the electrostatic repulsions between the cations, the q_m values for cadmium were not affected. Overall, the R^2 values from the C_e/q_e plots were much higher with the Freundlich model than the Langmuir model, which meant the process of adsorption occurred at the heterogenous sites on the surface of the adsorbents. This then showed the importance of applying the obtained adsorption data to the adsorption models in order to have a better understanding of the process that occurs. Furthermore, it showed how factors such as adsorbent concentration and pH have an effect on the parameters of the models.

Chemisorption is a selective, irreversible process in which electrons are transferred between an adsorbent and a metal ion. It is often distinguished by great selectivity and strong interaction when compared to physisorption. For example, iron oxides can remove lead from wastewater through Pb-Fe complexes, forming covalent or electrostatic interactions with the surface hydroxyl groups of $Fe(OH)_3$.

$$Fe(OH)_3 + Pb^{2+} \rightarrow Fe(OH)_3 - Pb^{2+} \tag{3}$$

The equation shows the binding of Pb^{2+} ions to the surface of ferric hydroxide, where the surface hydroxyl group (OH^-) serves as a location for Pb^{2+} binding.

Physisorption is the physical process by which metal ions are adsorbed onto adsorbent surfaces using weak van der Waals forces or electrostatic attraction. It is less selective than chemisorption, frequently reversible, and characterised by weaker contact forces such as van der Waals forces or hydrogen bonding. Physisorption occurs when copper (Cu^{2+}) ions are adsorbed on the surface of iron oxide. Metal ions may stick to the surface due to electrostatic interactions between positively charged metal ions and the negatively charged surface of iron oxide.

$$Fe_2O_3 + Cu^{2+} \rightarrow Fe_2O_3 \rightarrow Fe_2O_3 - Cu^{2+} \tag{4}$$

The equation shows the physical adsorption of Cu^{2+} ions on the surface of iron oxide, where the interaction is primarily electrostatic. The efficacy of adsorption in wastewater is influenced by pH, metal ion concentration, temperature and the composition of the adsorbent. Lower pH and larger metal ion concentrations promote adsorption.

2.2 Co-precipitation mechanisms

Co-precipitation is the process by which metal ions precipitate from a solution concurrently with iron hydroxides/oxides [9]. When new minerals are formed or iron hydroxides precipitate in the presence of the metals, iron oxides absorb the metal ions (such as Cd^{2+}, Pb^{2+} and As^{3+}). This process usually takes place when the pH of the solution is changed to encourage the precipitation of iron hydroxides and metal ions are either adsorbed onto the surface or integrated into the crystal structure.

The most common iron oxides/hydroxides involved in co-precipitation are ferrihydrite, goethite and haematite [10]. For example, when iron salts (such as $FeCl_3$) are added to water, they can be hydrolysed to form iron hydroxides that can trap metal ions. Additionally, it includes surface precipitation which occurs when heavy metal ions form insoluble compounds on the surface of iron oxides/hydroxides. Enhances the overall removal efficiency by combining adsorption and precipitation processes [11].

For example, when hydroxide ions (OH^-) are added to a solution containing heavy metals, metal hydroxides (such as $Fe(OH)_3$, $Cu(OH)_2$, or $Pb(OH)_2$) are formed. These hydroxides frequently co-precipitate with other metal ions, particularly if the metals have similar sizes or chemical properties.

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_{3(s)} + Cu^{2+} \rightarrow Cu(OH)_{2(s)} \tag{5}$$

Sulfide co-precipitation: When sulfide ions (S^{2-}) are introduced into the solution, metal sulfides can form. Many heavy metals form highly insoluble sulfides, and this method is particularly useful for removing metals like mercury (Hg), arsenic (As) and cadmium (Cd). Sulfide co-precipitation is one of the most effective methods for removing metals from wastewater, especially in acidic conditions.

$$Cd^{2+} + S^{2-} \rightarrow CdS_{(s)} \tag{6}$$

2.3 Redox reactions involving iron oxides/hydroxides

Iron oxides/hydroxides can undergo redox reactions in the presence of heavy metals, including arsenic, chromium and lead, lessening their chemical behaviour and potentially lowering their toxicity [12]. These reactions are necessary for converting metal species into less hazardous or more stable forms, aiding their removal. Arsenic reduction commonly occurs in two oxidation states in the environment: As^{5+} (oxidised) and As^{3+} (reduced). Iron oxides can help reduce As^{5+} to As^{3+} making it less mobile and potentially less hazardous [13]. This happens when electrons flow from iron oxide to arsenic species, changing their chemical behaviour and removing them from the aqueous phase. Chromium in its hexavalent form (Cr^{6+}) is highly toxic and mobile in the environment [14]. Iron oxides, particularly magnetite, can reduce Cr^{6+} to the less toxic and less mobile Cr^{3+} form through electron transfer. This reaction effectively removes chromium from contaminated water. Lead ions (Pb^{2+}) can be reduced to less soluble forms or adsorbed onto iron oxide surfaces, additionally, Pb^{2+} may form lead sulfide (PbS) precipitates when in the presence of sulfide ions, further enhancing the removal process [4, 11, 12].

$$Fe^0 + Pb^{2+} \rightarrow Fe^{2+} + Pb^0 \tag{7}$$

$$Cr^{6+} + Fe^0 \rightarrow Fe^{3+} + Cr^{3+} \tag{8}$$

3. Synthesis and surface modifications of iron oxides

Iron oxides/hydroxides are well known for their exceptional physicochemical characteristics, which enable them to remove heavy metals from wastewater with great efficiency [15]. These substances, which come in synthetic and natural forms, have superior adsorption properties. The creation of nano-structured versions and different surface changes, however, can greatly improve their performance. While maximising its use for large-scale wastewater treatment, these developments also solve the drawbacks of natural iron oxides [7]. Iron oxides are synthesised and modified for the removal of heavy metals using a variety of procedures, such as sol-gel, hydrothermal synthesis and co-precipitation, each of which affects the material's adsorption capacity, surface characteristics and crystallinity [16]. Certain analytical methods are necessary to completely comprehend these traits. While transmission electron microscopy (TEM) and scanning electron microscopy (SEM) offer information on particle size and shape, X-ray diffraction (XRD) establishes phase composition and crystallinity [17]. Functional groups involved in metal binding are identified by Fourier-transform infrared spectroscopy (FTIR), while surface chemistry and oxidation states are revealed by X-ray photoelectron spectroscopy (XPS). Furthermore, surface area and porosity are evaluated using Brunauer-Emmett-Teller (BET) analysis, which is essential for adsorption effectiveness [18]. Interpretation of these data helps establish structure-property relationships, optimise synthesis conditions and enhance heavy metal removal performance, thereby improving the practical applicability of iron oxides in wastewater treatment [17].

3.1 Natural vs. synthetic iron oxides

Haematite, magnetite and goethite are examples of natural iron oxides that are affordable and easily accessible, making them appropriate for simple heavy metal removal procedures [19]. However, the existence of contaminants and irregular surface characteristics frequently restrict their adsorption capacity. On the other hand, the adsorption efficiency of synthetic iron oxides can be greatly enhanced by customising them to have well-defined particle sizes, larger surface areas and optimised crystallinity [20]. To create synthetic iron oxides with excellent properties, techniques like sol-gel, hydrothermal synthesis and co-precipitation are frequently used. For large-scale applications, consistency and repeatability are crucial, and these controlled synthesis processes guarantee both [21].

3.2 Surface modifications for enhanced performance

Iron oxides/hydroxide interactions with heavy metals are significantly influenced by their surface characteristics [21, 22]. They can be made more adsorbent by surface changes, including coating with polymers, doping with other metals, or functionalisation with organic groups. Functional groups like hydroxyl (-OH) or carboxyl (-COOH), for instance, increase the binding sites for heavy metal ions, whereas doping with elements like cerium or manganese enhances the iron oxides/hydroxides' reactivity and selectivity [23]. Biocompatible polymer surface coating also improves stability under a range of pH and temperature settings in addition to improving adsorption. These changes increase the variety of wastewater conditions where iron oxides/hydroxides can be used successfully [24].

3.3 Nano-structured iron oxides for improved adsorption

The use of iron oxides in the removal of heavy metals has changed dramatically with the development of nanotechnology. Because of their distinct electrical characteristics and high surface area-to-volume ratio, nano-structured iron oxides/hydroxides have better adsorption capabilities than their bulk counterparts [25]. Magnetite (FeO_4) and maghemite (γ-Fe_2O_3) nanoparticles are especially good at adsorbing trace metals like arsenic, cadmium and lead. Additionally, their magnetic qualities make recovery and reuse simple, improving the treatment process's sustainability [26]. These nanostructures are made using sophisticated methods that provide exact control over size and shape, such as microwave-assisted synthesis and electrochemical deposition.

3.4 Challenges and mitigation strategies

Notwithstanding their benefits, using nano-structured and modified iron oxides has drawbacks, such as agglomeration, poor stability and possible environmental hazards from leaching nanoparticles [27]. Researchers are looking into composite materials that combine iron oxides with other matrices, such as graphene oxide, carbon nanotubes, or clay minerals, in order to overcome these problems [28]. These composites increase the adsorbents' overall mechanical and thermal stability in addition to improving dispersion [21].

3.5 Applications and future directions

Conventional wastewater treatment facilities are not the only facilities that use modified and synthesised iron oxides. They are being used more and more in sophisticated treatment systems like electrochemical cells and membrane reactors [27]. They are also being investigated for their potential to eliminate new pollutants, such as medications and personal hygiene items [19]. In order to develop more effective and sustainable water treatment options, future research is anticipated to concentrate on combining iron oxide-based adsorbents with renewable energy systems and real-time monitoring technologies [28]. Researchers and businesses can meet the increasing need for efficient heavy metal removal in wastewater by developing the synthesis and modification of iron oxides, which will greatly aid in resource recovery and environmental preservation [24].

4. Applications in heavy metal removal

Because of their high affinity for hazardous metal ions, affordability and environmental friendliness, iron oxides and hydroxides have been widely used to remove heavy metals from wastewater [29]. They are used in a variety of industries and deal with contaminants that are harmful to ecosystems and human health, such as arsenic, lead, chromium and cadmium [30]. Case studies of heavy metal removal, its effectiveness in systems contaminated by multiple metals, and their combination with other treatment techniques are highlighted in this section.

4.1 Case studies of arsenic, selenium and cadmium removal

It has been shown that iron oxides/hydroxides, specifically goethite (α-FeOOH) and haematite (α-Fe_2O_3), can efficiently remove arsenic through co-precipitation and adsorption. For example, a study conducted in China used iron hydroxide nanopetalines adsorbents for the removal of arsenic from water, with a removal efficiency of 67% [30]. Because of their excellent performance and durability, iron hydroxide nanopetalines might be regarded as a viable material for removing arsenic from As-contaminated water, according to the research's new approach for the production of arsenic immobilisation materials [30]. A study in Spain investigated iron oxide and hydroxide nanoparticles for the removal of selenium oxyanions due to their high adsorption capacity [26]. By altering the impregnation technique, which is based on oxidative hydrolysis with $FeSO_4$ $7H_2O$ and CH_3COONa, and the kind of carbonaceous support (activated carbon or sucrose-based carbon foam), the study assessed the phase and morphology of the iron nanoparticles, which are important factors in Se adsorption. Scanning electron microscopy was used to examine the distribution and shape of the iron nanoparticles, while XRD was used to identify the iron species. Their study's uniqueness and goal were to create a carbon material impregnated with various iron phases, such as hydroxides (goethite/lepidocrocite) and oxides (magnetite/haematite), that could remove both Se^{4+} and Se^{6+}. The findings demonstrated that Se^{4+} adsorption is more advantageous on magnetic hydroxides (71%) and oxides (78%), as opposed to haematite (<40%) [26]. A study by Shah and Ghafoor (2023), evaluated the effectiveness of iron oxide nanoparticles in removing cadmium ions from food and water samples. Numerous methods, such as dynamic light scattering, zeta potential, FTIR, SEM, XRD, BET and vibrating sample magnetometer, were used to characterise their samples. The sorption efficacy of freshly synthesised sorbent was examined in relation to several variables, including pH, temperature, sorbent amount, sonication time and sample and eluent volume. The central composite design was used to optimise the relevant elements, while the Plackett–Burman design was used to identify the important factors for the microextraction of the target analyte. Under ideal circumstances, $Fe_3O_4@SiO_2@APTES$ maintained over 96% analyte recoveries and showed good stability even after more than 80 adsorption/desorption cycles [24]. Nano-structured iron oxides have demonstrated exceptional adsorption capabilities in the removal of cadmium, which makes them appropriate for treating wastewater from battery production facilities that contain cadmium.

The case studies on the use of iron hydroxides to remove heavy metals from wastewater demonstrated the efficiency of different iron-based adsorbents, such as goethite, haematite and magnetite, in binding and removing contaminants through adsorption, co-precipitation and redox reactions [31]. However, a deeper analysis of their surface structures, including specific surface area, pore size distribution, and functional groups, is crucial to understanding their adsorption mechanisms. The structural and chemical changes that occur during metal adsorption can be better understood by using analytical techniques like XRD for phase identification, SEM for morphological analysis, FTIR for functional group characterisation and XPS for oxidation state determination [21]. In order to analyse adsorption data and ascertain the effectiveness and reusability of these materials, kinetic and isotherm models, such as the Langmuir and Freundlich models are also frequently employed [15].

4.2 Applications in multi-metal polluted systems

Multiple heavy metals are frequently present in real-world wastewater streams, making selective removal difficult. Because iron oxides can adsorb a variety of metal ions at once, they are useful in systems that are polluted by many metals [26]. For instance, mining effluents containing a combination of arsenic, lead and cadmium have been treated with magnetite nanoparticles, which have demonstrated significant removal efficiency for all pollutants [22]. Iron oxides/hydroxides' vast surface area and adaptable surface functional groups, which promote multi-ion adsorption, give them a synergistic impact when binding several metals. Competitive adsorption between ions, however, can lower efficiency, highlighting the necessity of optimisation in these kinds of systems [19].

4.3 Integration with other treatment methods

One possible tactic to improve heavy metal removal is the use of iron oxides with other treatment technologies [7]. It has been demonstrated that combining membrane filtration systems with iron oxide/hydroxide adsorption enhances water quality while lowering fouling. In addition, iron oxides/hydroxides heavy metal adsorption capabilities are enhanced by their usage as catalysts in advanced oxidation processes (AOPs), which quicken the degradation of organic contaminants. The recovery of important metals is made possible by hybrid systems, such as electrochemical reactors combined with iron oxide adsorbents, which further improve the removal efficiency of metals like lead and chromium [28].

4.4 Field applications and scalability

Iron oxides/hydroxides have proven to be durable and scalable in a variety of wastewater treatment settings through field applications [32]. For example, thousands of households in rural areas could now have access to clean drinking water thanks to pilot-scale systems that use ferric hydroxide to remove arsenic [30]. Similarly, to combat lead and cadmium contamination, industrial wastewater treatment plants have implemented integrated treatment systems that use iron oxide-coated sand filters. These systems can be implemented on a broad scale because they are frequently low maintenance and energy efficient [27].

4.5 Future directions and environmental implications

The development of reusable and multipurpose adsorbents is key to the future of iron oxide/hydroxide applications in heavy metal removal [27]. Iron oxide/hydroxide nanoparticles may be efficiently recovered and reused due to emerging technologies like magnetic separation, which lowers waste production. Furthermore, iron oxides combined with renewable energy-powered systems like solar-powered treatment units offer long-term solutions for isolated and resource-constrained locations [29]. Iron oxide-based adsorbents' long-term sustainability and environmental safety will be further guaranteed by research into lifecycle evaluation. Iron oxides/hydroxides continue to be essential in reducing heavy metal contamination in wastewater and promoting sustainable water management techniques by addressing particular case studies, improving performance in intricate systems, and combining with cutting-edge treatment techniques [21, 22, 27]. **Table 3** discusses the benefits, difficulties, and practical uses of iron oxides and hydroxides in wastewater treatment, while showcasing their adaptability in eliminating a variety of heavy metals and pollutants.

5. Performance evaluation

Heavy metals can be effectively removed from water by iron oxides and hydroxides, although oxidation and agglomeration might limit their efficacy [33]. However, a number of methods are available to enhance their performance, like employing them in composites or mixing them with other materials. Evaluating their performance for removing heavy metals from wastewater is an important area of research in environmental science and engineering as every metal oxide has advantages and drawbacks that affect its suitability for particular heavy metal removal capabilities [33].

Application area	Iron oxide type	Target heavy metals	Mechanism	Advantages	Challenges	Examples	References
Adsorption in Wastewater	Magnetite, Haematite, Goethite	Pb, Cd, Cr, As	Surface binding *via* ion exchange and complexation	High adsorption capacity, selective removal	Potential saturation requires regeneration	Use in industrial wastewater treatment	[24, 30]
Magnetic Separation	Magnetite	As, Hg, Zn	Magnetic properties facilitate easy recovery	Reusable, environmentally friendly	Loss of magnetic properties over time	Treatment of mining effluents	[23]
Catalytic Reduction	Nano-structured Iron Oxides	Cr^{6+}	Redox reactions catalysed by iron species	High efficiency at low concentrations	Requires precise synthesis control	Conversion of Cr^{6+} to Cr^{3+}	[29]
Composite Materials	Iron Oxide-Graphene, Iron Oxide-Clay	Pb, Cu, Ni	Enhanced surface area and binding affinity	Synergistic effects improved stability	Cost of composite material preparation	Removal of metals in mixed contaminants	[32]
Electrochemical Applications	Modified Magnetite	Pb, Cu	Electro-assisted adsorption	Energy efficient, adaptable to various pH	Electrodes prone to fouling	Electrochemical water treatment reactors	[27]
Membrane Filtration Systems	Iron Oxide-Coated Membranes	Cd, As, Se	Adsorption-enhanced filtration	Integration with existing systems	Membrane fouling, replacement cost	Hybrid filtration-adsorption units	[26]
Emerging Contaminant Removal	Nano Iron Oxides	Pharmaceuticals, Personal Care Products	Adsorption and catalytic degradation	Versatile for new pollutants	Uncertainty about long-term impacts	Municipal wastewater pilot studies	[19]

Table 3.
Iron oxides and hydroxides in removing a wide range of heavy metals and contaminants.

Research in this area frequently includes experimental studies to measure adsorption capacities, batch and column tests to simulate real-world conditions, and computational modelling to predict adsorption behaviour. The study is mostly centralised on the use of electrodes for wastewater treatment, however, the development degree is less, and the basis for waste water treatment is seen in **Figure 1**. The study proves that the performance evaluation of iron is currently neglected for wastewater treatment.

5.1 Adsorption capacity and efficiency

The ability of metal oxides to adsorb heavy metals onto their surface is known as adsorption capacity (q_e) (Eq. (9)) and it measures the degree to which liquids, gases, or dissolved solids adhere to surfaces such as rocks (**Table 4**) [34].

$$q_e = (C_0 - C_e) \times \frac{v}{m} \tag{9}$$

where v is the volume of the solution, m is the amount of adsorbent and C_0 and C_e are the concentrations of the material before and after adsorption. Adsorption capabilities are frequently improved by increased surface area and specific surface chemistry, which iron oxides/hydroxides such as goethite, haematite, magnetite and ferrihydrite possess [35]. Their adsorption capacity depends on a number of variables, including the specific metal ion, pH, competing ions and the characteristics of the iron oxide/hydroxide [36]. The adsorption mechanism is categorised by two processes. Firstly, surface complexation whereby the inner- or outer-sphere complexes of the metal ions attach to hydroxyl groups on the surface of iron oxides/hydroxides [37]. Secondly, metal cations take the place of protons or other ions, such as Na^+ and

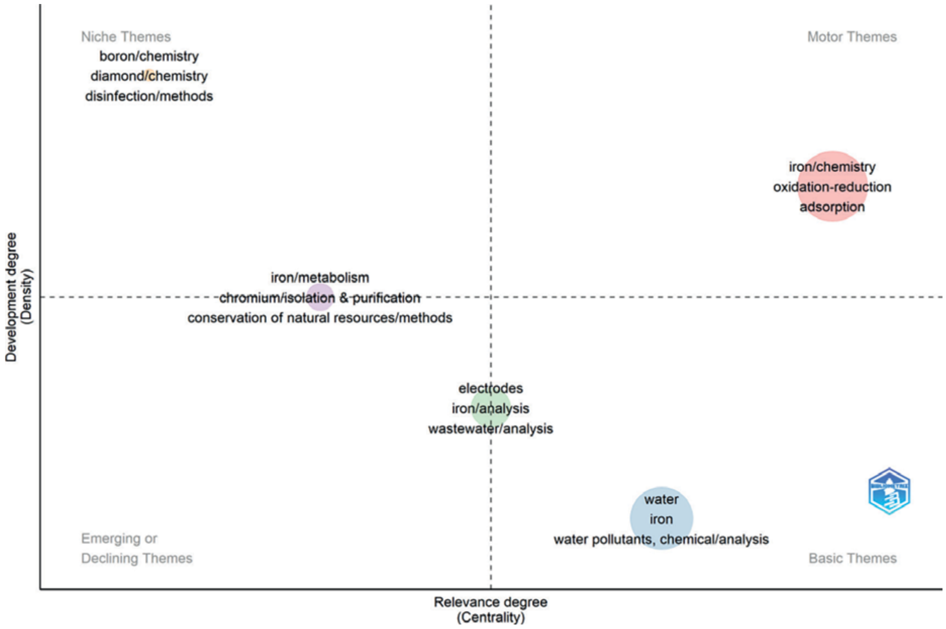

Figure 1.
The performance evaluation of the development degree versus the relevance degree of the iron oxides application in wastewater treatment.

Metal ion	Adsorbent type	Adsorption capacity (mg/g)
Lead (Pb^{2+})	Ferrihydrite	50–200
Cadmium (Cd^{2+})	Goethite	10–50
Chromium (Cr^{6+})	Magnetite	30–100
Copper (Cu^{2+})	Haematite	10–80
Arsenic (As^{3+})	Ferrihydrite	20–90
Zinc (Zn^{2+})	Amorphous Fe oxide	5–50

Table 4.
Adsorption capacities of various iron metals on different metal ions.

K^+ and lastly, electrostatic attraction at particular pH values, positively charged metal ions are drawn to the negatively charged surfaces of iron oxides [38].

A number of operational and ecological variables, including acidity, temperature, competing ions and ionic strength, affect how well iron oxides remove heavy metals from wastewater [33]. The most important factor influencing adsorption efficacy is pH since it determines the chemical form of heavy metals. Parameters such as the surface charge of iron oxides are amphoteric, their surface charge varies with pH. Positively charged surfaces at low pH repel metal cations while adsorbing anions such as arsenate or chromate. Negatively charged surfaces at high pH promote metal cation adsorption, and for iron oxides, a pH of 6–8 is typical. For instance, at low pH values, lead (Pb) precipitates as $Pb(OH)^{2+}$, whereas at high pH values, it forms soluble Pb^{2+}. At low pH, chromium (Cr) occurs as Cr^{6+} oxyanions (such as $HCrO^{4-}$) and as Cr^{3+}. For maximal adsorption, each metal has an ideal pH range. Temperature influences reaction kinetics and thermodynamics, which in turn impacts the adsorption process [34]. Adsorption kinetics by decreasing viscosity and increasing molecular mobility, higher temperatures frequently accelerate the diffusion and adsorption of heavy metals. There are two possible adsorption processes, firstly exothermic at higher temperatures, adsorption diminishes (e.g., arsenic removal on goethite) [39]. Endothermic as observed for some cations, such as Cu^{2+} on magnetite, adsorption rises with temperature [40]. While too high temperatures might promote adsorbent leaching or alter the structure of iron oxides, moderate temperature increases (20–40°C) typically improve adsorption.

The concentration of dissolved salts in the solution is known as its ionic strength, and it influences the performance of adsorbates [41]. Iron oxide and metal ion electrostatic attraction is screened by high ionic strength, which may lower cation adsorption effectiveness. Adsorption sites may be occupied by competing ions (such as Na^+, Ca^{2+}, Cl^- and $SO_4{}^{2-}$) that prevent heavy metal uptake. Since oxyanion adsorption uses more robust surface complexation mechanisms, it is less impacted (e.g., arsenate, chromate). Complex interactions are frequently the result of the combined effects of pH, temperature and ionic strength [42]. Due to competition from other ions, the effect of pH on adsorption may be decreased at high ionic strength. Through an increase in reaction kinetics, elevated temperatures can counteract the effects of ionic strength.

5.2 Reusability and regeneration of iron-based adsorbents

Iron-based adsorbent's economic viability and practical use in wastewater treatment are largely determined by their regeneration and reusability [6]. By ensuring

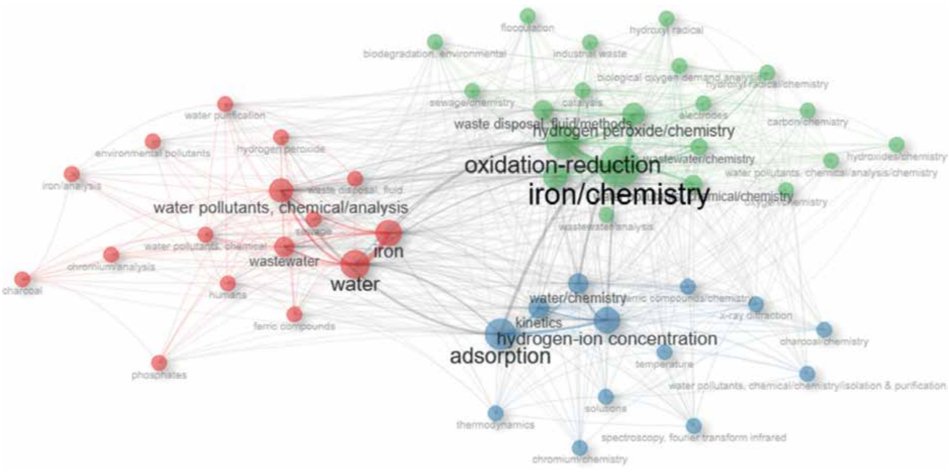

Figure 2.
A schematic diagram of the visualisation network on the different applications of iron metal oxide.

that the adsorbents maintain their adsorption capability over several cycles, efficient regeneration techniques minimise waste and operational expenses. The benefits include cost-efficiency, sustainability and performance maintenance to make sure that removal efficiency remains constant across several cycles. Restoring active sites and removing heavy metals from the iron-based adsorbent surface area are the goals of the regeneration process [43]. Typical techniques consist of acid washing for chemical regeneration by protonating surface sites and desorbing heavy metals (Pb^{2+}) using acids like HCl, HNO_3, or H_2SO_4 [44]. However, using too much acid can dissolve the adsorbent and shorten its lifespan. Alkaline cleaning is done by deprotonating surface sites, alkaline solutions (such as NaOH) are employed to desorb oxyanions like chromate or arsenate.

Regeneration by heat, when adsorption is reversible, heating the adsorbent to high temperatures (200–500°C) can desorb heavy metals. This is efficient for pollutants that are co-adsorbed with metals and are organic or thermally decomposable. However, elevated temperatures have the potential to change the structure of the adsorbent (e.g., ferrihydrite crystallising into haematite) [45]. Regeneration *via* electrochemistry applies redox processes as seen in the visualisation network in **Figure 2** below, applying an electric potential to the adsorbent might encourage desorption [46]. Through adsorption-regeneration cycles using a cathodic method, the material also showed good stability; after eight consecutive cycles, its adsorption capacity was nearly fully recovered. After the cycles, the removal percentage was maintained at about 80%. Limitations include the need for infrastructure and high energy usage. Combination techniques regeneration efficiency can be increased by combining techniques (such as chemical and thermal), particularly for complicated wastewater compositions [47].

6. Comparative analysis

Iron hydroxides and oxides have shown great promise as adsorbents for heavy metal removal from wastewater because of their distinct physicochemical characteristics. The cost, effectiveness and environmental impact of iron oxides are clearly superior to those of more conventional adsorbents such as zeolites and activated carbon [25]. The vast surface area of activated carbon makes it very effective, but it can be costly to create and needs a lot of regeneration after saturation [16]. Comparably, zeolites have strong ion exchange qualities but are less efficient with some heavy metals, such as chromium and arsenic [25]. On the other hand, iron oxides, especially when they are nano-structured or altered, show excellent selectivity for a variety of metals, such as chromium, lead and arsenic, *via* processes such as ion exchange, surface complexation and redox reactions [18].

The environmental friendliness of iron hydroxides and oxides is one of their main benefits [19]. Iron oxides can frequently be obtained from natural or recycled sources, in contrast to zeolites, which may require considerable energy for synthesis, and activated carbon, which might produce secondary waste during regeneration [29]. Furthermore, some iron oxides, such as magnetite, have magnetic characteristics that make it simple to separate and recover from aqueous systems, which lowers operational complexity. They are also very reusable due to their magnetic recoverability, which further increases their affordability for industrial uses [21].

Iron oxides do have certain drawbacks, though. Their efficacy in practical applications may be diminished by variables that affect their adsorption capability, including pH, competing ions and the presence of organic matter [20]. Additionally, despite their improved adsorption capabilities, nano-structured iron oxides have difficulties with regard to scalability for large-scale applications and possible environmental toxicity [5]. However, although being more expensive, activated carbon continues

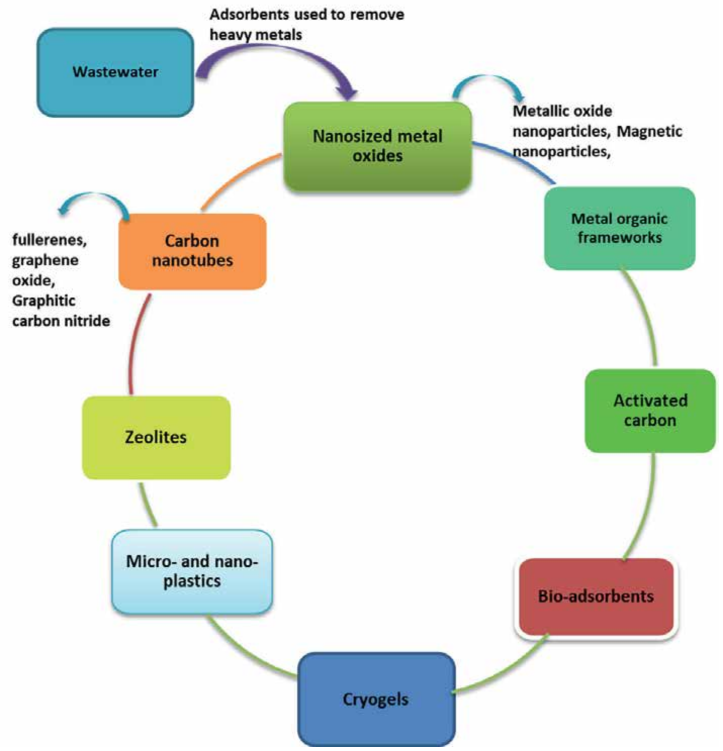

Figure 3.
Different adsorbents for removal of heavy metals from wastewater.

to function consistently across a wider range of circumstances [25]. In extremely salty conditions, where iron oxides may show reduced adsorption, zeolites perform exceptionally well [29]. **Figure 3** illustrates the different adsorbents that are used to extract heavy metals from wastewater.

Notwithstanding these difficulties, improvements in iron oxide surface modification have greatly increased their range of applications. Their stability and affinity for the target pollutants have been enhanced by coating them with functional groups or combining them with other materials like graphene or charcoal [30]. Because of these changes, iron oxides are now highly competitive adsorbents for treating wastewater, especially in applications that call for the selective removal of metals like chromium and arsenic, which are harder for zeolites or activated carbon to remove [20]. In comparison to other popular adsorbents, **Table 5** lists the advantages and disadvantages

Parameter	Iron oxides/hydroxides	Activated carbon	Zeolites
Adsorption Capacity	High for specific heavy metals (e.g., As, Pb, Cr) due to surface complexation	Generally high but less selective for heavy metals	Moderate, dependent on metal type and zeolite structure
Selectivity	Selective for oxyanions and specific cations	Non-selective adsorbs a wide range of organic and inorganic pollutants	Selective for certain ions based on pore size and charge
Regeneration	Requires chemical or thermal methods, regeneration efficiency may decrease over time	Reusable after thermal/chemical treatment, but performance may degrade	Can be regenerated with saline solutions, stable over cycles
Cost	Moderate, especially for naturally occurring forms	High due to production and activation processes	Moderate, depending on synthesis or natural availability
Environmental Impact	Environmentally benign can be used in natural or nano-structured forms	Sustainable if sourced from waste materials but production can be energy-intensive	Sustainable, especially natural zeolites, but mining may cause disruption
Surface Area	Moderate to high (especially nano-structured forms)	Very high, enhancing adsorption of various contaminants	Moderate, optimised for ion exchange
pH Sensitivity	Effective in acidic to neutral pH ranges	Broad pH applicability	Limited in very acidic or basic conditions
Mechanism	Surface complexation, ion exchange, redox activity	Adsorption on porous surface	Ion exchange within zeolite structure
Ease of Use	Easily integrated into water treatment systems	Requires pre-treatment in some cases	Readily available but may require pre-conditioning
Applications	Heavy metal removal, catalytic degradation of contaminants	Removal of organic pollutants, some heavy metals	Ion exchange for ammonium, heavy metals, and radioactive ions
Limitations	Prone to fouling, loss of efficiency after multiple regeneration cycles	High cost, effectiveness decreases with specific metals	Pore clogging, selectivity limitations for mixed contaminants

Table 5.
Comparative analysis of iron oxides and hydroxides vs. other adsorbents [29].

of iron oxides and hydroxides, highlighting their potential for specific heavy metal removal applications while tackling issues like regeneration and selectivity. Several studies have reported differing removal efficiency and cost implications for techniques such as membrane filtration, activated carbon and iron oxide-based adsorption [20, 27]. In contrast to membrane filtration, which can achieve comparable or higher efficiencies but has much higher operating costs, often more than 92,91 ZAR per cubic metre, iron oxide-based adsorbents, for example, have shown heavy metal removal efficiencies exceeding 80% at an estimated cost of 1.86 ZAR to 18.49 ZAR per cubic metre [20, 27, 48].

7. Environmental implications

The use of iron oxides and hydroxides for the removal of heavy metals from wastewater is a widely studied and applied method due to their ability to adsorb a variety of toxic metals [49]. However, while this method has significant environmental benefits, there are also potential concerns and implications to consider [4].

7.1 Assessment of environmental safety and sustainability

Assessing the environmental safety and sustainability of using iron oxides and hydroxides to remove heavy metals from wastewater is crucial to understanding both the effectiveness and long-term impact of this approach [49]. Iron ions are generally not toxic at low concentrations, but excess release can cause water discoloration and reduced oxygen levels, affecting aquatic life. Iron oxides can also leach heavy metals, posing environmental hazards. Proper handling and disposal of spent adsorbents are crucial to prevent contamination and ensure long-term environmental risk. The ability of iron oxides/hydroxides to be regenerated and reused enhances their sustainability and reduces their environmental impact. The energy consumption of iron oxide adsorbents is critical to their sustainability, as they use less energy than other sophisticated wastewater treatment methods, lowering operational costs and carbon footprint [49].

7.2 Impact on ecosystems and water bodies

While these materials can successfully remove heavy metals from water, improve water quality and alter water chemistry, they can also potentially affect aquatic organisms [2]. Additionally, they can precipitate metals, potentially entering the food chain and altering benthic habitats [50]. Iron oxides/hydroxides negatively impact ecosystems and water bodies through improper disposal of its waste, the inability to reuse them in other heavy metal removal means they are going into waste [11]. The improper disposal of this waste can disrupt local ecosystems, promote algae growth and deplete oxygen levels, which then highlights the need of continue developing more environmentally friendly methods.

8. Future trends and innovations

Enhancing the effectiveness, sustainability and scalability of iron-based adsorbents for the removal of heavy metals from wastewater is the main goal of future developments and trends in this field. The goal of research and development is to overcome current constraints, including difficulties with regeneration, selectivity and performance in intricate water matrices.

8.1 Advances in nanotechnology for iron-based adsorbents

Nanotechnology is an emerging technology that is being used in many different fields due to its distinct morphological and physicochemical characteristics [51]. Nanomaterials have been utilised in environmental cleanup because of their minuscule size and shape. Using the remarkable adsorption properties of nanoparticles, nanomaterials have shown to be a promising approach. Nanomembranes have many benefits, most notably their wettability, notwithstanding their sporadic fouling.

Compared to conventional wastewater treatment techniques, nanotechnology has several advantages. Most importantly, it is capable of eliminating pollutants such as heavy metals, organic chemicals, microorganisms and emerging substances [52]. Secondly, it generates less waste and uses less energy in contrast to traditional techniques. Iron oxide nanoparticles (IONPs) include haematite (α-Fe_2O_3), magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3) [53]. Nanoparticles of zero-valent iron (nZVI) have high reductive potential, able to immobilise heavy metals and decompose organic pollutants solvents [54]. Moreover, magnetic nano-adsorbents based on iron use external magnetic fields to make recovery simple. Nanocomposites based on iron, for improved performance, hybrid materials combine carbon (such as graphene oxide or carbon nanotubes), polymers, or other metal oxides [55]. Nano-adsorbents based on iron offer higher surface area meaning there are more adsorption-active sites. Finally, they can interact with contaminants quickly and effectively due to their nanoscale size. Because of their qualities and versatility, iron-based nano-adsorbents are a potential class of materials for environmentally friendly, sustainable solutions.

8.2 Hybrid systems combining iron oxides with other materials

Adsorption technology has advanced significantly with hybrid systems that combine iron oxides with other materials. These systems combine complementary elements to improve performance, selectivity and stability while utilising the inherent qualities of iron oxides, such as magnetism, strong surface reactivity, and affinity for specific metals [56]. Hybrids based on carbon iron oxide and activated carbon combine the reactivity and magnetism of iron oxides with the adsorption ability of activated carbon and are used to eliminate colours, heavy metals and organic contaminants [57]. In a hybrid of iron and graphene oxide (GO), the adsorption and catalytic qualities of iron oxides are enhanced by graphene oxide's high surface area, superior conductivity and robust mechanical strength [58]. Applications of such hybrids include photocatalysis for pollutant degradation and the adsorption of metal ions and medicines. With regards to carbon nanotubes (CNTs) coupled to iron oxides, CNTs' high adsorption capacity, and iron oxide's magnetic characteristics work together to facilitate recovery, and applications include cleaning up oil spills, pigments and heavy metals [59]. Hybrids based on polymers include iron oxide and monomers (such as polyvinyl alcohol, polyethylene glycol and chitosan). Furthermore, iron oxides can be coupled to materials such as biochar, silica and cellulose, which all bring advantages such as increased porosity, the addition of more functional groups, increasing hydrophilicity and biocompatibility. This then allows the iron oxides to be applied to a wide range of pollutants such as antibiotics and insecticides.

The impact of hybrid technologies includes enhanced adsorption, enhanced selectivity, magnetic recovery, durability, stability and multifunctionality. Some challenges include cost and scalability, environmental impact and reusability. A state-of-the-art method for tackling intricate industrial and environmental problems is the use of hybrid systems that combine iron oxides with other materials to provide high-performance, multipurpose solutions.

8.3 Smart adsorbents with tunable properties

Smart adsorbents with tunable characteristics are innovative materials designed to dynamically react to environmental stimuli, such as pH, temperature, light, or magnetic fields [60]. These materials are perfect for industrial applications, water treatment and environmental remediation because they provide improved selectivity, reusability and efficiency in adsorption operations. Essential elements of smart adsorbents are that they respond to particular triggers by modifying adsorption capacity or releasing pollutants [61]. Tunable surface chemistry targets particular contaminants and the functional groups on the adsorbent surface can be altered. For ion oxides, the smart adsorbent mechanism is obtained by coating hydrogels, metal-organic framework and polymers on them which is then pH-responsive, and can change their surface charge and adsorption capacity [62]. Applications include the elimination of organic dyes, phosphate and heavy metals, including chromium and arsenic [63].

9. Conclusion

Iron oxides/hydroxides have gained a lot of momentum and coverage in the wastewater remediation area for their use as an adsorbent in the adsorption of heavy metals such as lead, chromium and arsenic. Their ability to be modified to adapt to environmental conditions, sufficient surface area and their physical properties make them essential for the removal of heavy metals in water. The ongoing research of wastewater remediation has allowed for these materials to be effectively integrated with other materials such as nanomaterials and monomers, which further enhances their heavy metal adsorption capabilities. This Study showed that iron oxides can achieve heavy metal removal efficiencies of over 80%, with operational costs ranging from 1.86 to 18.49 ZAR per cubic metre of treated water, depending on the process and contaminant load. Moreover, the regeneration and reuse potential of iron-based adsorbents can significantly reduce waste production and lower long-term treatment costs. Future advancements in nano-structured iron oxides may further improve removal efficiency while optimising economic viability. Iron oxides/hydroxides favours the environment to a certain extent through their ability to be regenerated after adsorption cycles and reused. This implies that the need to continuously make these materials is decreased and there is a decrease in reagent use and energy consumption. Given that the adsorption of heavy metals from wastewater using iron oxides/hydroxides is a simple and low cost technique, it allows for the upscaling of their applications in industry, including at wastewater treatment plants. This in general, further benefits the environment as the water released is of better quality in terms of heavy metals pollution, without containing harsh chemicals that would impact on the aquatic environment.

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Conflicts of interest

The authors declare no conflict of interest.

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Chapter 5

Sustainability of Carbon Mineralisation and Utilisation in the Mineral Processing Industry: Challenges and Future Perspectives

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Abstract

The energy-intensive aspect of the mineral processing industry and its dependence on fossil fuels present substantial hurdles in minimising greenhouse gas emissions. The industry contributes significantly to global emissions; thus, adopting cutting-edge technologies and practices is required to mitigate the detrimental impact on the environment. Multifaceted challenges such as technological, regulatory aspects, and social and environmental implications present prospects for innovation and improvement, which could culminate comprehensive strategies for effective management. This study examines green mining initiatives that have a positive economic impact as well as trends in green technologies and sustainable practices that provide avenues to reduce emissions and enhance sustainability through improved energy efficiency and transportation emissions. A broader basic implementation of carbon capture and utilisation technologies requires significant investment and development. The practicality of carbon capture and mineralisation to mitigate carbon dioxide emissions by converting gaseous carbon dioxide into stable carbonate minerals contributes to circular economy and environmental advantages. On the other hand, carbon market holds significant economic advantages through the sale of carbon credits and by-products. This study further emphasises importance of coordinated efforts across industry, government, and communities to overcome existing barriers and accomplish significant carbon emission reductions.

Keywords: carbon mineralisation technologies, mineral processing industry, carbon dioxide emissions, climate change, carbon market, carbon capture and storage

1. Introduction

The mineral processing sector is a fundamental component of the world economy, indispensable to the extraction and refinement of various vital minerals. The principal role of this business is to transform raw ores into precious minerals and metals, necessary for the innumerable commodities for the advancement of technologies to improve wealth and health of humankind [1]. The extractive metallurgy and processing of valuable minerals is a crucial component of the mining industry. This process involves several procedures and equipment aimed at extracting precious minerals from waste, enhancing the quality of the extracted minerals, and ensuring effective recovery. The mining and mineral processing sectors significantly contribute to a nation's economy while providing essential resources for contemporary society. This industry is vital for sustainable economic development and total growth domestic product growth. Mineral exploration is the initial phase in the mining value chain, preceding mining and mineral processing, with the final product mostly being high-value minerals gained through metallurgical processes [2, 3]. The mineral processing industry faces a multitude of challenges ranging from energy consumption and risk management to the integration of new technologies and environmental concerns. The loss of biodiversity and social disruption due to land use change, pollution and water depletion, and other wastes-related mining and mineral processing impose the greatest debilitating issues in this industry. Each of these areas presents unique obstacles that require innovative solutions and strategic planning to overcome [4]. For instance, emissions of significant amount of greenhouse gas (GHG) emanating from energy-intensive mining and other processing activities account for about 10% of global emissions [5]. In particular, the carbon dioxide (CO_2) emissions from burning coal and oil have been regarded as an influential driver of global warming, which are closely related to the harmful effects of climate change [6]. Recently, the emission of CO_2 has been up to 40 billion tonnes annually as a result of human and industrial activities. The energy-intensive nature of mineral processing, particularly in comminution operations, contributes to the existing environmental challenges. This is because of variability in ore quality affects the energy efficiency of crushing and screening processes, necessitating robust technological advancements that could influence efficiency and sustainability. Despite the existence of measures to mitigate prominent environmental catastrophes, these initiatives often prioritise immediate risk management above long-term sustainability. The summary of issues highlights the complexity of sustaining practices in the mineral processing industry. Addressing these challenges requires comprehensive approaches that include cooperative efforts among governments, stringent protections, investment in sustainable technology, and significant stakeholder engagement [7].

Within the mining and mineral deposits processing sectors, sustainability has emerged as one of the most potent forces influencing industry growth [8]. These sectors mining can significantly be impacted by the digital technology revolution and affordable energy from renewable sources. These revolutions could play key role from mining of mineral deposits processing of various ores and extraction of high-value metals and also not limited to secondary resources like electronic waste [2]. The use of digital mining technologies and innovative practices is essential for improving energy conservation and emission reduction. These technologies facilitate better resource management and operational efficiency, leading to a more sustainable mining industry. The basic essence of industrial enterprise is fast changing due to the digital revolution. The initiation of cloud computing and the Internet of Things as well as significant developments and breakthroughs in various research fields, including artificial intelligence, machine learning and big data analytics, robotics, autonomy, drones, three-dimension printing, sensor technologies, and electricity generation based on renewable energy, portend several disruptive changes [2]. While the mineral processing industry is essential for economic development, it must prioritise sustainable practices to address its environmental and health impacts. Balancing resource extraction and processing with environmental responsibility remains a significant challenge that requires technological advancement industry. Green mining initiatives are increasingly recognised for their potential to positively impact both the environment and the economy. These initiatives focus on reducing emissions, enhancing sustainability, and improving energy efficiency, thus leading to the economic benefits, improved resource efficiency and reduction of operational costs within the mining sector. For instance, the adoption of green supply chain management practices has been shown to sustain the economic performance of mining firms by optimising resource use and minimising waste [1]. By integrating green technologies and sustainable practices, mining operations can achieve significant reductions in greenhouse gas (GHG) emissions and energy consumption, while also boosting economic efficiency and promoting carbon mineralisation. Green mining initiatives and carbon mineralisation are pivotal in addressing environmental challenges associated with mining and CO_2 emissions. These initiatives aim to integrate sustainable practices into mining operations, reducing carbon footprints while enhancing resource recovery. Carbon mineralisation, in particular, offers a promising method for CO_2 sequestration by converting CO_2 into stable mineral carbonates, which can be integrated into mining processes to achieve both environmental and economic benefits. These initiatives leverage mining waste and industrial by-products to sequester CO_2 thus contributing to both waste management and emissions reduction.

Carbon mineralisation is a promising approach for addressing CO_2 emissions, one of the primary contributors to global climate change. This natural process, which is sped up by industrial uses, creates stable carbonate minerals by reacting CO_2 with mineral substrates like calcium or magnesium silicates [9]. Carbon mineralisation presents a technique to sequester CO_2 in the mineral processing business, but it also opens the door to using carbonates as valuable resources in agriculture, construction, and other fields [10]. However, minimising environmental effects while striking a balance between a number of variables, such as energy efficiency, process scalability, and economic viability, is necessary to achieve sustainable carbon mineralisation in this sector [11].

The emphasis on sustainable methods to slow down climate change has increased due to the growing concern over greenhouse gas (GHG) emissions, especially CO_2 [12]. One viable method for lowering atmospheric CO_2 levels is carbon mineralisation, which is the process of absorbing CO_2 and turning it into stable mineral carbonates. In addition to providing long-term carbon sequestration, this method supports the sustainable practices required by the mineral processing sector, which contributes significantly to greenhouse gas emissions [13]. In addition to addressing environmental issues, carbon mineralisation promotes the creation of novel by-products that can benefit various sectors by leveraging naturally occurring minerals such as silicates that are rich in calcium and magnesium [14]. Conversely, carbon utilisation enhances mineralisation by looking into ways to turn CO_2 into useful items like chemicals, fuels, and building materials [15]. By connecting environmental objectives with financial incentives, this two-pronged strategy improves the circularity of carbon use [16]. Additionally, in order to reduce its environmental impact and support global climate goals, the mineral processing industry must implement carbon mineralisation and utilisation procedures [14]. This chapter explores the significance of these technologies; looking at how they promote sustainability, their possible uses, and the opportunities and problems, they pose for the future of climate change mitigation and mineral processing.

2. Exploration of carbon mineralisation

Massive efforts have been made in recent years towards the development of technologies to mitigate global climate change through carbon capture and storage (CCS). A different method to reduce CO_2 from the atmosphere is related to CO_2 capture by injecting it into mid-ocean depth to dissolve it. Nevertheless, highly stored CO_2 is unreliable, there is possible leakage, and CO_2 eventually returns to the environment [17]. Carbon mineralisation is an intriguing option for long-term CO_2 reduction [18]. It involves the reaction of CO_2 with metal oxides or silicates to generate stable carbonates [19]. During carbon mineralisation, CO_2 comes into contact with mineral-rich calcium (Ca) and magnesium (Mg) and reacts to carbonate minerals such as dolomite ($CaMgCO_3$) and calcite (calcium carbonate ($CaCO_3$)), and host metastable hydrated carbonates, which includes hydromagnesite, dypingite, nesquehonite, hydrolcite to name the few. This method draws attention to its ability to store CO_2 in stable minerals over time and the spontaneity of the reaction under normal conditions. CO_2 mineralisation is an economical way to lower the emission of GHG, unlike other carbon capture technologies that require significant amounts of energy and reagents [20].

2.1 Carbonation pathways and mechanism in industrial application

The carbon mineralisation strategy has sparked substantial interest as a green and low-carbon method of treatment for CO_2 emissions [21]. Mineral CO_2 sequestration in industrial applications is usually studied in the context of ultramafic minerals found in mine tailing. By definition, ultramafic and mafic minerals/rock are comprised of high magnesium (Mg) and iron (Fe) content found in the earth's mantle, which make them superb candidates for mineral CO_2 sequestration (i.e. mineral carbonation). The typical examples of minerals with the characteristics of ultramafic rocks that have demonstrate to sequester CO_2 are olive ne $(Mg, Fe)_2SiO_4$, clinopyroxene Ca, Mg, Fe, Na) (Mg, Fe, Al) $(Si, Al)_2O_6$, and pyroxene ($CaMgSi_2O_6$) [20]. **Figure 1** below, amended following the previous literature review update, depicts the numerous carbonation routes that were investigated [22]. Carbon dioxide mineralisation routes are categorised as neither

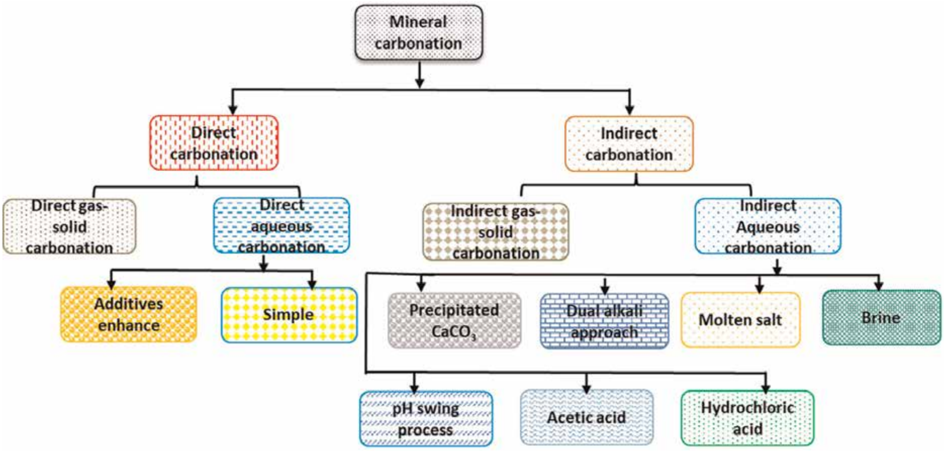

Figure 1.
Schematic illustration of different mineral carbonation (CO_2 sequestration) routes.

indirect carbonation nor direct. The direct CO_2 mineralisation happens when the aforementioned process occurs in one step to form carbonate products [21]. Indirect mineral carbonation includes the numerous steps where the divalent cations are extracted from the host mineral and converted into reactive species oxide.

2.1.1 Direct mineral carbonation

Direct carbonation represents a straightforward method for mineral carbonation, where a suitable feedstock, such as serpentine or Ca/Mg-rich residues, undergoes carbonation in a single-step process [23]. In this process, the CO_2 is fed into a reactor where it gets into contact and reacts with minerals (feedstock). This approach integrates metal extraction and CO_2 reaction within the same reactor, enhancing efficiency and sustainability in carbon sequestration [24]. Moreover, direct CO_2 mineralisation refers to the circumstance when metal dissolution and mineral CO_2 sequestration occur concurrently in one reactor. In this method, the high pressure (340 bar) and temperature (500°C) are crucial to achieve optimal carbonation rates to maximise the conversion rate in single-step gas-solid carbonation. This process (direct carbonation) occurs in an aqueous environment which involves three steps: (i) direct aqueous carbonation, (ii) direct gas gas-solid carbonation, and (iii) precipitation of a product carbonate.

2.1.2 Direct gas-solid carbonation

This is the simplest CO_2 sequestration process. The direct gas-solid phase carbonation process, while theoretically spontaneous due to a negative Gibbs free energy, necessitates significant energy input, such as high-temperature steam or electricity, to improve reaction kinetics and efficiency. This process involves the reaction of CO_2 with alkaline residues, and many parameters influence the carbonation rate. Additionally, the process of direct gas-solid mineral carbonation methods is thermodynamically favourable (exothermic), as evidenced by negative Gibbs free energy values, implying spontaneity under optimal conditions. The advantage of the exothermic reaction nature of direct gas-solid phase carbonation is that the energy release can be utilised (harnessed) in various applications [25].

2.1.3 Direct aqueous CO_2 mineralisation

Direct aqueous CO_2 mineralisation is the carbon dioxide reaction with minerals or trash in the liquid phase. Unlike the gas-solid interaction, direct aqueous carbonation entails an interaction between gas, liquid, and solid, as indicated *via* Eqs. (1)–(3). Gibbs free energy (ΔG^0 in $kjmol^{-1}$) was calculated according to ΔG^0, where the value of G determines whether the reaction processed spontaneously. According to the previous studies, the negative values in Eqs. (1) and (2), the reactions occur thermodynamically favourable, implying the spontaneously in water. Nonetheless, Eq. (3) indicates the positive ΔG^0 which implies less favorible under ambient conditions.

$$CO_{2(2)} + H_2O(l) \rightarrow H_2CO_{3(aq)}\ \Delta G^0 \approx -84\ kJMol^{-1} \tag{1}$$

$$H_2CO_{3(aq)} \rightarrow H^+ + HCO_3^-\ \Delta G^0 \approx -5.7\ kJMol^{-1} \tag{2}$$

$$H^+ + HCO_3^- \rightarrow H^+ + CO_3^{2-}\ \Delta G^0 \approx 2.9\ kJMol^{-1} \tag{3}$$

Furthermore, the reaction process has three steps: (1) CO_2 dissolves in solution, (2) Ca^{2+} and Mg^{2+} are leached from minerals or trash, and (3) CO_2 reacts with Ca^{2+} and Mg^{2+} to generate precipitates. The presence of water enhances CO_2 capture effectiveness in environmental settings. Direct aqueous CO_2 mineralisation (carbonation) can enhance conversion and reaction rate by optimising reaction conditions, using high gravity methods, and employing ultrasonic techniques [21].

2.1.4 Indirect mineral carbonation

Indirect CO_2 mineralisation (carbonation) approaches are essentially multi-step procedure with independent metal dissolution and carbonation reactions in various reactors under varying conditions [26]. In addition to indirect and direct CO_2 mineralisation pathways, brines can also be used as a source of divalent cations such as Fe^{2+}, Mg^{2+}, and Ca^{2+}. Because changes in characteristics are closely connected to injectivity, storage capacity, and stability during geological CO_2 storage, the carbon mineralisation mechanism should be considered when designing an optimal carbon capture and storage solution [27].

Carbon mineralisation consists of three major processes. These processes include (i) dissolution of CO_2 in water which is thermodynamic favourable with Gibbs free energy of $\Delta G^0 \approx -631.6$ kJMol^{-1}, (ii) dissolution of carbonate or silicate minerals $\Delta G^0 \approx -174.1$ kJMol^{-1}, and (iii) precipitation of carbonate minerals. As indicated in **Figure 2** and Eq. (4), the pressurised CO_2 gets dissolved in water to produce the carbonic acid, which ultimately dissociates into anions like carbonate ($CO_3{}^{2-}$) $\Delta G^0 \approx -529.8$ kJMol^{-1} and bicarbonate ($HCO_3{}^{-}$) $\Delta G^0 \approx 260.4$ kJMol^{-1} $G^0 \approx 10.5$ kJMol^{-1}.

$$CO_{2(g)} + H_2O(l) \leftrightarrow H_2CO_{3(aq)} H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow H^+ + CO_3^{2-} \Delta G^0 \approx -529.8\ \mathrm{kJMol}^{-1} \quad (4)$$

The steps displayed in **Figure 2** provide the reactive carbonate species, which are necessary for mineral carbonation. Additionally, these reactions are influenced by temperature, pressure, and the physical state of the reactants and can all affect reaction kinetics.

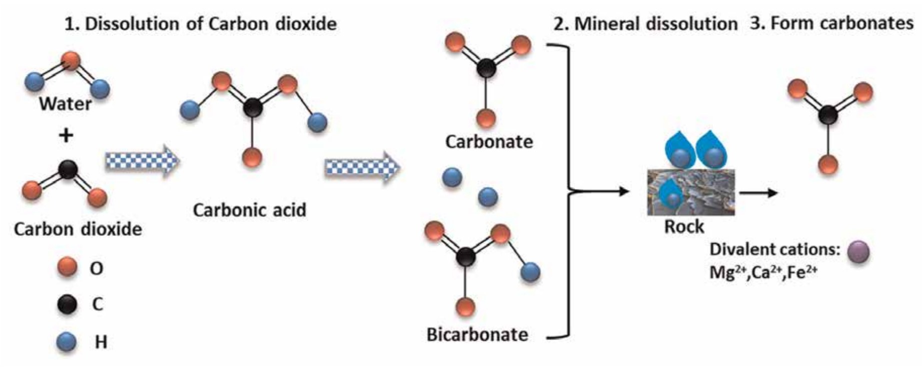

Figure 2.
Carbon mineralisation process through dissociation of CO_2 in water.

Aspect	Indirect mineral carbonation	Direct aqueous CO_2 mineralisation
Steps	Multi-step process	Single-step reaction
Reaction medium	Separate extraction and reaction steps	Aqueous media solution
Performance efficiency	Higher efficiency based on optimised steps	Lower kinetics
Complexity	Require extraction reagents	Few steps process
Applicability	Suitable for a greater variety of minerals.	Performs effectively with minerals that are very reactive

Table 1.
Key differences between indirect aqueous carbonation and direct CO_2 mineralisation.

2.1.5 Indirect aqueous carbonation

Indirect aqueous carbonation is a potential technology for carbon capture and utilisation that uses a variety of industrial by-products and additives to improve the carbonation process. This method involves dissolving calcium-rich materials in an aqueous solution and then reacting them with CO_2 to generate stable carbonates, typically calcium carbonate ($CaCO_3$) [28]. In this process, coal fly ash is the source of calcium and the additives such as aspartic acid and sucros are used to enhance calcium leaching and carbonation efficiency, which enhances the entire process. Gasos et al. reported the indirect CO_2 mineralisation of recycled concrete aggregate (RCA), in which calcium is first leached into an aqueous ammonium nitrate solution, followed by carbonation to yield high-purity precipitated $CaCO_3$. The proposed schematic for indirect aqueous carbonation is illustrated in **Figure 2**. **Table 1** illustrates and stipulates the key difference between the above-mentioned direct aqueous carbonation and indirect mineral carbonation.

2.2 *In situ* carbon mineralisation and *ex situ* carbonation

In situ carbon mineralisation is the procedure of converting carbon dioxide into stabilised minerals in subterranean geological formations. This process takes place in subsurface geological structures due to the transition of silicate minerals into carbonates (i.e. $CaCO_3$ and $MgCO_3$) [6]. It is classified into two basic categories depending on CO_2 reaction with (i) iron (Fe) or aluminium oxide (Al_2O_3) and calcium or magnesium silicates. However, the shortcoming associated with this process is that it requires a long period of time like hundreds of years for a complete mineralisation in contrast to other existing CO_2 storage methods. As illustrated in **Figure 3(a)**, geological underground formations with sufficient porosity and permeability, which originally contained oil and gas, can operate as the target formations for long-term CO_2 storage [29, 30], while *ex situ* CO_2 mineralisation needs CO_2 and a feedstock that comprises metal ions to sequester CO_2 as thermodynamically stable carbonates. As illustrated in **Figure 3(b)**, CO_2 can be collected and concentrated from flue gas streams of industrial focal points such as steel, cement, and power plants [26]. Carbonisation feedstocks might be geological or anthropogenic. Natural resource feedstocks, such as ultramafic rocks containing magnesium-silicate minerals, are preferred due to their high conversion rates. However, ultramafic rocks have more reserves than wollastonite. There has been an increasing interest in using

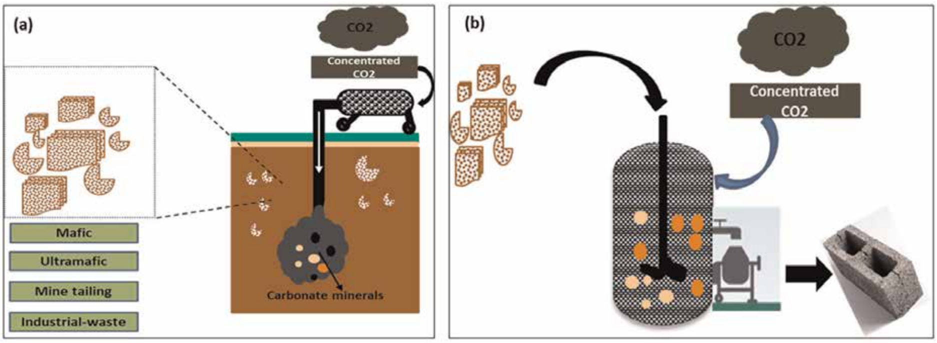

Figure 3.
Schematic illustration of (a) in situ *carbonation and (b)* ex situ *mineralisation process.*

anthropogenic feedstock for mineral carbonation. The industrial wastes such as iron and steel slags and coal fly ashes represent affordable sources of alkali and alkaline earth metals, which mitigate waste disposal. Additionally, other anthropogenic sources of alkali metals such as magnesium are mine tailing from raw materials industries. The waste (rock residues) that contains calcium minerals or magnesium-silicate minerals from the operation of mines are being used for both direct and indirect mineral carbonation pathways. Moreover, the mantle peridotite and ultramafic intrusions are examples of magnesium-rich, calcium-bearing rocks that are extremely reactive [3]. These are an important source of alkalinity for the Mt. to Gt storage of CO_2 through carbon mineralisation.

Among ultramafic rocks, olivine and wollastonite are minerals that play a crucial part in carbonation processes. These processes involve the reaction of minerals with CO_2 to generate stable carbonates. The following subsections explain the thorough breakdown of wollastonite and olivine:

2.2.1 Olivine (forsterite) carbonation

The olivine reaction is a promising carbon sequestration mechanism that converts atmospheric carbon dioxide into stable mineral form. The olivine (silicate mineral) normally reacts with CO_2 and produces the secondary mineral, including carbonates such as magnesium carbonates ($MgCO_3$) and iron magnates ($FeCO_3$) as illustrated in Eqs. (5)–(12) [31]. This procedure takes advantage of the inherent reactivity of olivine, a magnesium silicate mineral, to aid in the mineralisation of CO_2. The subsequent sections detail the major components of this system [32]. Olivine is one of the promising candidates for CO_2 storage; however, olivine carbonation is hindered by the slow reaction rate at room temperature, which requires extremely high temperatures and pressures to trigger the carbonation. We numerously attempted in the previous studies to enhance the olivine carbonation. Saleh et al. reported the enhanced dissolution of olivine using the wet supercritical environments which indicated the fast rate of CO_2 mineralisation at 90–150°C and 2–9 MPa [33]. The overall forsterite carbonation reaction (Eq. (12)) is thermodynamically favourable with Gibbs free energy of $\Delta G^0 \approx -73.8\ \mathrm{kJMol^{-1}}$ which indicates that it proceeds spontaneously according to Eqs. (5)–(11).

$$Mg_2SiO_4 + 4H^+ \rightarrow 2Mg^{2+} + H_4SiO_4\ \Delta G^0 \approx -162.9\ \mathrm{kJMol^{-1}} \tag{5}$$

$$H_4SiO_4 = SiO_{2(am)} + H_2O\ \Delta G^0 \approx 209.8\ \text{kJMol}^{-1} \tag{6}$$

$$2CO_{2(g)} = 2CO_{2(aq)}\ \ \Delta G^0 \approx 17.0\ \text{kJMol}^{-1} \tag{7}$$

$$2CO_{2(aq)} + 2H_2O = 2HCO_3^- + 2H^+\ \Delta G^0 \approx 72.2\ \text{kJMol}^{-1} \tag{8}$$

$$2HCO_3^- = 2CO_3^{2-} + 2H^+\ \Delta G^0 \approx 118.0\ \text{kJMol}^{-1} \tag{9}$$

$$2CO_3^{2-} + 2Mg^{2+} \rightarrow 2MgCO_3\ \Delta G^0 \approx -90.8\ \text{kJMol}^{-1} \tag{10}$$

$$Mg_2SiO_4 + 2CO_2 \rightarrow 2MgCO_3 + SiO_2\ \Delta G^0 \approx -73.8\ \text{kJMol}^{-1} \tag{11}$$

As displayed in Eqs. (5)–(11), the mineral carbonation steps begin with the amorphous silicate mineral by dissolving and releasing divalent cations (Mg, Ca, Fe), additionally to silica (SiO_2) in the form of silicic acid formation. H_4SiO_4 species then precipitate as amorphous SiO_2 at lower temperatures. In the following step, carbon dioxide dissolves concurrently, creating carbonic acid, bicarbonate ions, and carbonate ions in varying quantities depending on pH. The dissolved magnesium ions react with bicarbonate and carbonate ions to generate carbonate minerals, which precipitate at high saturation indices [31].

2.2.2 Pyroxenes (diopside) and wollastonite carbonation

Pyroxene carbonation, specifically $CaMgSi_2O_6$ (diopside), is a complicated process that takes place under variable pressure and temperature conditions. According to research, these reactions have a considerable influence on melting processes in geological environments, particularly in ultramatic subduction zones and the mantle [34]. Carbonates found in carbonated ultramafic rocks and supra-subduction mantle may survive subduction beyond subarc areas. This mechanism is important for natural carbon sequestration, as well as understanding weathering and the carbon cycle.

The generalised reaction of pyroxene in subterranean geological formations is illustrated as follows in Eq. (12). According to Gibbs free energy value for pyroxene carbonation reaction suggests the spontaneous reaction.

$$CaMgSi_2O_6 + 2CO_2 + H_2O \rightarrow CaCO_3 + MgCO_3 + 2SiO_2\ \Delta G^0 \approx -472.1\ \text{kJMol}^{-1} \tag{12}$$

While wollastonite interacts with CO_2, producing $CaCO_3$ and SiO_2. This reaction demonstrates a mineral carbonation process, which is relevant to CO_2 sequestration and capture technologies. The reaction can be summarised as follows in Eq. (14), forming a non-spontaneous reaction according to overall Gibbs free energy in Eq. (13).

$$CaMgSi_2 + 2CO_2 \rightarrow CaCO_3 + SiO_2\ \Delta G^0 \approx 4.8\text{kJMol}^{-1} \tag{13}$$

The temperature, pressure, and the presence of acidic surroundings all have a substantial impact on wollastonite carbonation, which speeds up the reaction. Elevated temperatures (25–200°C) and pressures (1–200 bar) promote the solubility of calcium, a critical component in the carbonation process, resulting in improved CO_2 sequestration effectiveness. Additionally, injecting weak acids can improve the reaction conditions [35].

2.2.3 Serpentine carbonation

Serpentine ($Mg_3Si_2O_5(OH)_4$) carbonation is a chemical reaction in which serpentine combines with CO_2 to create magnesium carbonate (e.g., magnesite and $MgCO_3$) and silica. This method is crucial for carbon sequestration and mineral carbonation because it permanently binds CO_2 into stable solid minerals. The general reaction can be expressed as in Eq. (14) which implies non-spontaneous reaction:

$$Mg_3Si_2O_5(OH)_4 + 3CO_2 \rightarrow MgCO_3 + SiO_2 + 2H_2O \ \Delta G^0 \approx 1177.24 \text{ kJMol}^{-1} \quad (14)$$

Serpentine is essential and abundant in ultramafic rocks, thus making it a good choice for CO_2 capture and storage. The reaction between CO_2 and serpentine converts greenhouse gas into a stable mineral.

2.3 Process engineering

Grinding and activation procedures dramatically increase the reactivity of minerals by expanding their surface area and changing their crystal structures. Several methods, including mechanical, thermal, and chemical activations, have been investigated to optimise mineral performance for applications like as construction materials and environmental remediation. The effects of these activation mechanisms include the mechanical activation (i.e.) particle size reduction and enhanced reactivity, thermal activation (i.e. temperature effects and phase transformation), and chemical activation (i.e. optimal combinations) [36].

2.4 Other carbon dioxide sequester approach: Application of LDO and LDH for CO_2 conversion into value-added chemicals

Layered double hydroxides (LDHs) are synthetic materials, which are utilised as catalyst precursors and layered double oxides (LDO)-based electrocatalysts. These materials have a potential role for carbon sequestration, specifically through carbon dioxide reduction reaction (CO_2RR) due to its tunable surface compositions and high specific area [37]. However, achieving predictable product selectivity from electrochemical carbon dioxide reduction remains tough because of difficulties in managing the oxidation states of metal (Cu, Ni etc.) versus robust structural reconstructive during the CO_2 electrochemical reduction reaction. The product selectivity and efficiency of CO_2RR are strongly affected by the catalyst nature, morphology, particle shape/size, and surface-composition among others thing [38]. Support is also an important factor. Current research has focused on LDO-Ni-based catalysts, which has demonstrated exceptional catalytic performance for electrochemical reduction of CO_2 to CH_3OH with up to 80% faradaic efficiency. Metal-LDH and Metal-LDO have proven to be an intriguing principle rationale for developing innovative catalyst for CO_2 reduction. Lu et al. achieved outstanding catalytic performance for CO_2RR to CH_3OH utilising a Cu-based LDH catalyst material [39, 40]. In past 10 years, bimetallic Cu-Ni-, Cu-In-, and Cu-Sn-based LDH/LDO exhibited more efficient for and C1 molecules (CO, H_2, CH_4) [41], which could transform to methanol and C_2 (C_2H_4, ethanol) as compared to monometallic Cu- and Sn-based LDH [42]. Recent research focuses on transition metal-based electrocatalyst nanostructures, categorised by selectivity: HCOO- (Pb, Sn, In), hydrocarbon selective (Cu), and CO selectivity (Pd). The functionalisation of Pd with various

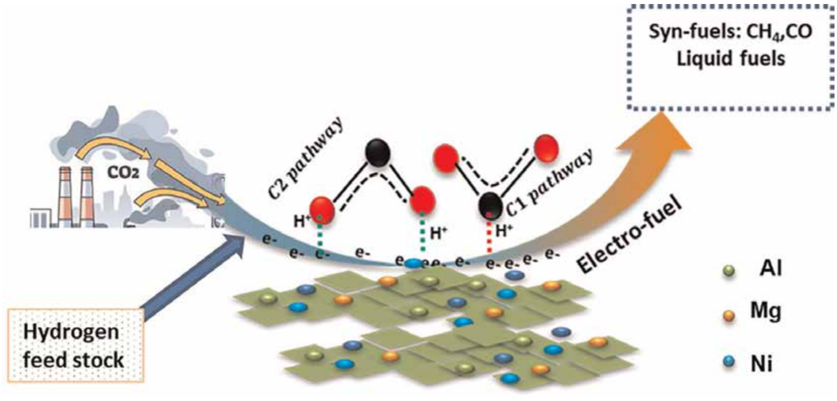

Figure 4.
Schematic illustration of carbon sequestration via *electron transfer during carbon dioxide reduction at the presence of LDH/LDO.*

Catalyst material	Synthetic route	Conversion reaction	Electrolyte	Syngas selectivity	Refs.
Ru-MgAlOx	Co-precipitation	Electrochemical reduction	$KHCO_3$	CO, 75%	[45]
Ni-LDO (MgAl)	Co-precipitation	—	—	72%CO_2R, 99 Selectivity	[46]
CuMgAl (LDH)	Hydrothermal synthesis	Electrochemical reduction	$KHCO_3$	CH_4, C_2+ products	[47]
ZnAlLDH	Facile co-precipitation	Electrochemical reduction	$KHCO_3$,sat CO_2	CO	[48]
CoAl-LDH	Urea hydrolysis	—	—	—	[49]
ZnMLDH	Microwave-assisted hydrothermal	Photocatalytic conversion	H_2O	CH_3OH	[50]

Table 2.
Summary of catalyst application for carbon dioxide reduction reaction.

nanomaterials has received significant attention and demonstrated superior selectivity and activity of CO2RR towards C1 (methanol [43]), CO (syngas) relatively conversion to C_2 (EtOH) compounds [44]. **Figure 4** shows the C_1 and C_2 routes during CO_2 conversion into value-added compounds (**Table 2**).

3. Critical analysis of reviewed literature

Carbon capture and utilisation (CCU) technologies have demonstrated varying levels of success in real-world applications across the mining and industrial sectors [16, 51]. One prominent example is the carbonation of waste rock and mine tailings to sequester CO_2, in which minerals rich in calcium and magnesium react with carbon dioxide to generate stable carbonates. A study by Molahid et al. [51] examined the effects of several parameters on the carbonation of Fe-rich mine waste materials in order to sequester CO_2 by mineral carbonation. The findings showed that waste samples' alkaline pH made them appropriate for the carbonation process. Iron and calcium oxides (39.58–62.95%) were found in wastes, according to the chemical composition, suggesting a high potential for carbon sequestration. The carbon absorption capacity analysis showed that 81.7–87.6 g CO_2/kg of trash was sequestered at alkaline pH (8–12). These results have shown the considerable potential for using Fe-rich mine waste as a feedstock for mineral carbonation [51]. Cherepovitsyna et al. [52] examined the CCU Projects managed by oil and gas companies in Russia. The study examined how oil and gas corporations developed the entire CCU cycle and evaluated the projects economic feasibility. The results show that, in comparison with traditional methanol, which costs about USD 400 per tonne, the predicted minimum price for CO_2-based methanol to accomplish project payback is USD 1128 per tonne [52]. Furthermore, Dutta et al. [14] evaluated the potential of using CO_2 with a combined framework for chemical and electricity productions.

Additionally, projects like CarbonCure, which adds collected CO_2 to concrete during manufacturing to increase strength and lower carbon intensity, have helped CCU gain traction in the cement sector [53]. The scalability of such solutions is highlighted in literature evaluations, with some pilot programs effectively lowering emissions by 5–7% [14, 16, 54]. Nonetheless, detractors contend that the integration of CCU systems into current supply chains and the availability of high-purity CO_2 sources limit their wider deployment. Life cycle assessments (LCAs) also show that although using CO_2 can lower emissions, the energy sources used for compression and collection have a significant impact on the overall environmental benefits [55]. Johnsson et al. [10] examined the industrial CO_2 capture and storage cost curve for marginal abatement using a Swedish case study. The study took into account variations in the necessary investment and the possibility of utilising surplus heat to meet the steam demand of the capture process. With a cost varying from about 40 €/t CO_2 to 110 €/t CO_2, depending on the emission source, CO_2 capture deployed to 28 industrial units captures CO_2 emissions that account for about 50% of Sweden's total CO_2 emissions (from all sectors), according to the marginal abatement cost curve (MACC) [10]. Bose et al. [56] examined novel strategies for CCS as essential steps to lower emissions in industrial sectors. A thorough analysis of case studies from around the world is provided for both the successful execution of CCS projects and the evaluation of their environmental effects.

Innovative CCU strategies, such turning CO_2 into synthetic fuels or chemicals, have also being investigated by the steel sector [57]. Garcia and colleagues [58] conducted a comparison of CO_2 storage and utilisation by improving sustainability through the integration of renewable energy. Their research highlighted how CCU technology could help the shift to a sustainable energy system by lowering future CO_2 emissions through the conversion of captured CO_2 into useful fuels and chemicals. According to their findings, prospective CCU technologies have the potential to considerably reduce greenhouse gas emissions if green hydrogen becomes more inexpensive, even though CCS methods are more developed [58]. In addition, one well-known example is the Steelanol project, which is supported by the European Union and turns waste gases and collected CO_2 from the manufacture of steel into ethanol [57]. This initiative illustrates the possibility for generating income streams from waste gases, but it also draws attention to the difficulties associated with maintaining product purity, expensive equipment, and intricate infrastructure needs [11].

Direct air capture (DAC) technologies are becoming more and more popular in the mining industry as supplementary methods to conventional carbon mineralisation [59]. A study by Ozkan et al. [59] assessed the foundations and present state of DAC technology. The existing state of commercial DAC technologies was detailed in their review, which also explained the five pillars of technology: capture methods, their energy requirements, ultimate costs, environmental effects, and political backing. With DAC's 0.01 Mt. CO_2/year capture capability, it will be difficult to fulfil the carbon capture rates outlined in the Paris Agreement's goals for 1.5–2°C global warming. DAC may, however, help offset some of the hard-to-avoid annual emissions from transportation (24%), iron-steel sector (11%), wildfires (0.8%), and concrete (8%) [59]. Cao et al. [60] examined a reactive separation method for pre-combustion CO_2 capture based on carbon molecular sieve membranes (CMSM). They investigated a hybrid system that combines an adsorptive reactor (AR) and a membrane reactor (MR), with the feed for the AR being the reject stream from the MR. According to the study's findings, the MR-AR system based on CMSM is a promising technique for producing clean electricity [60]. The studied literature does, however, highlight some serious disadvantages, such as the high energy requirements of DAC systems and the viability of expanding such programs without major subsidies [59]. The practical uses of carbon CCU in a range of industries are compiled in **Table 3**, which also highlight the results, difficulties, and corroborating sources for critical analysis.

Case study/ industry	Application	Technology/ process	Outcomes	Challenges identified	References
Mining sector: Nickel refining	CO_2 sequestration in tailings	Carbonation of mine tailings using CO_2	Achieved CO_2 sequestration efficiency; production of stable carbonates.	High water and energy requirements; long reaction times.	[61]
Cement manufacturing	Utilisation of CO_2 in cement sector	Accelerated carbonation curing	Sequestered significant CO_2 per unit mass.	Limited scalability due to cost and infrastructure constraints.	[62]
Steel industry	Conversion of CO_2 into fuels	Use of bio-electrochemical processes	Produced methane and ethanol; reduced carbon footprint.	Low efficiency and high operational costs of bio-electrochemical systems.	[62, 63]
Power plants: coal-fired	Mineralisation of fly ash	CO_2 injection into fly ash for carbonate formation	Produced usable construction materials.	Variable quality of carbonates produced; high initial setup costs.	[12]
Chemical manufacturing	CO_2 as a raw material for chemical synthesis	Use of CO_2 to produce methanol and urea	Substantial reduction in greenhouse gas emissions.	High-pressure requirements and dependency on renewable energy sources.	[14]
Mining: gold mining waste	Neutralisation of acid mine drainage	Integration of CO_2 for carbonate precipitation	Improved water quality; reduced heavy metal contamination..	Slow reaction kinetics and high CO_2 supply demand.	[54]
Wastewater treatment plants	CO_2 utilisation in nutrient recovery	(Ca)-rich effluent of a phosphorus (P) recovery system	Nutrient recovery from wastewater.	Land use requirements and optimisation of algae strains.	[13]

Table 3.
Summary of real-world applications of carbon capture and utilisation across industries.

4. Economic and environmental considerations of carbon mineralisation

4.1 Cost and feasibility

Comprehensive techno-economic assessments are necessary to evaluate the feasibility and profitability of different mineralisation processes. These assessments must balance capital expenses, operating expenses and potential income from by-products. Developing suitable products from the mineralisation process that can substitute conventional products is critical for economic viability. Life cycle assessment provides insights into the environmental and economic impacts of carbon mineralisation over the entire lifecycle, helping to identify areas for cost reduction and efficiency improvements. The cost-effectiveness for indirect aqueous carbonation is anticipated to be economically viable, with prices ranging from $116 to 133 per tonne of CO_2 sequestered. In addition, this approach, which involves the chemical reaction of CO_2 with minerals, offers promise in lowering GHG emissions while remaining economically viable. Particularly, the economic viability of mineral carbonation techniques is predicted to cost between $50 and $300 per tonne of CO_2, with studies indicating a more favourable range of $116–133 per tonne [64, 65]. Waste management, by using industrial residues such as metallurgical slags, coal ash in carbon mineralisation reduces the need for waste treatment and landfilling, leading to cost savings for industries. Energy efficiency although the process is energy intensive, advancements in technology and process optimisation can lead to increased energy efficiency, further reducing operational costs. Improving the efficiency of the carbonation process through technological advancements can reduce costs [66, 67]. Techniques such as supercritical carbonation, microwave irradiation, and the use of additives have shown promise in enhancing reaction rates and reducing energy consumption [68]. Combining mineral carbonation with existing mineral processing operations can lower overall costs by utilising waste materials and reducing the need for additional raw materials.

4.1.1 Market potential

Carbon mineralisation is considered the most secure form of carbon sequestration, reducing the risk of CO_2 leakage. This enhanced security can elevate the value of carbon credits generated from mineralisation initiatives, as they require less monitoring and carry a lower risk of forfeiture [69]. The introduction of dependable carbon credits from these projects has the potential to reshape the pricing landscape of the carbon market. As these credits gain recognition for their reliability, they may command premium prices, thereby influencing the delicate balance of supply and demand [70]. Moreover, carbon mineralisation can transform industrial by-products into valuable construction materials, such as carbonated blocks, providing a viable alternative to conventional concrete [71, 72]. This not only generates marketable products but also contributes to a reduced carbon footprint in the construction sector. Techniques like aqueous carbonation can yield high-purity materials, including carbonates, silica, and iron oxides, which serve diverse industrial purposes [73]. These products can be sold in niche markets, potentially generating significant revenue. The process can also yield high-purity products such as magnesium and nickel carbonates, which are valuable in various industries [74, 75]. By incorporating circular economy principles, such as using steel slags for mineral carbonation, industries can achieve long-term stable carbon sequestration and create a more sustainable value chain. The sequestration of CO_2 through mineralisation can generate carbon credits, which can be traded in carbon markets, providing an additional revenue stream. Governments may offer tax incentives for companies that adopt carbon capture and utilisation technologies, further enhancing the economic viability of these projects. As governments impose stricter regulations on carbon emissions, adopting carbon mineralisation technologies can help companies comply with these regulations, avoiding potential fines and penalties. The secure nature of carbon mineralisation may prompt regulatory bodies to favour these projects, potentially leading to policy reforms that can prioritise mineralisation-based credits and enhance the credibility and attractiveness of carbon offset programs [76, 77].

4.1.2 Environmental considerations

Carbon mineralisation offers several potential environmental benefits when applied within the mineral processing industry. These benefits are primarily derived from the process of converting CO_2 into stable carbonates using industrial by-products, which can then be used in different applications [78]. Carbon mineralisation converts CO_2 into thermodynamically stable solid carbonates, effectively sequestering the carbon and preventing it from contributing to atmospheric greenhouse gas levels [72]. The process can significantly reduce the carbon footprint of industries by storing CO_2 and potentially avoiding more emissions than just storing CO_2 alone. Industrial residues such as metallurgical slags, incineration ashes, and mining tailings can be used as feedstock for mineral carbonation, thus reducing the need for waste treatment and landfilling [79]. The carbonates produced can be used in construction materials, substituting conventional products like Portland cement, which further reduces environmental impacts. Although the process requires energy, advancements in energy efficiency and the use of renewable energy sources can mitigate this drawback [80]. Increasing the energy efficiency of the mineral carbonation process is crucial to maximising its environmental benefits. By using industrial by-products, the need for mining and processing virgin materials is reduced, which in turn lowers the environmental impact associated with resource extraction. The high energy demand required to overcome slow reaction kinetics is a significant challenge. Improving the energy efficiency of the process is essential to fully realise its environmental benefits. Carbon mineralisation in the mineral processing industry presents a promising route for climate change mitigation by sequestering CO_2 and utilising industrial by-products. The environmental benefits include reduced greenhouse gas emissions, valorisation of waste materials, and the production of marketable construction products [81]. However, addressing the energy demands and optimising the process are critical to maximising these benefits.

4.2 Challenges and considerations

One of the main challenges of carbon mineralisation is the high energy demand required to overcome slow reaction kinetics. This can impact the overall economic feasibility unless energy-efficient methods are developed. The scalability of mineral carbonation processes from lab-scale to industrial-scale is crucial. The high initial cost of carbon mineralisation technology can be prohibitive. However, long-term benefits such as reduced carbon taxes and potential revenue from by-products can offset these costs. These techno-economic viability and life cycle assessments could identify hotspots and optimise process parameters to enhance sustainability and economic

Aspect	Economic considerations	Environmental considerations
Costs	• High initial and operational costs [83] • Indirect aqueous carbonation costing range of \$116–133/tonne	• Energy-intensive processes [80] • Reduction of waste treatment and landfilling
Benefits	• Market for carbonated products, carbon credits [72] • Enhanced energy efficiency, further reducing operational costs	• Permanent CO_2 storage, negative carbon footprint [80] • Reduction for the need of raw materials
Feasibility tools	• Techno-economic analysis [84] • Mineral carbonation techniques ranging \$116–133/tonne	• Life cycle assessments [71]
Resource utilisation	• Valorisation of by-products, reducing traditional material use [80]	• Application of industrial by-products, reducing waste [81]
Policy recommendations	• Support through carbon credits and tax incentives [69] • Impose stricter regulations on carbon emissions	• Implementation of CO_2 valorisation networks, enhancing energy efficiency [80] • Enhance credibility and attractiveness of carbon offset programs [76, 77].

Table 4.
Summary of economic and environmental considerations.

performance [80, 82]. Continued research and development are essential to overcome technical challenges, improve process efficiency, and reduce costs, enabling carbon mineralisation a viable option for the mineral processing industry. **Table 4** summarises economic and environmental considerations.

5. Conclusion and future perspective

One of the main setbacks to large-scale scale-up of aqueous mineral carbonation is the high energy requirement and operational cost associated with the process. The slow kinetics and low carbonation capacity of available feedstocks, such as mining tailings and industrial wastes, are significant obstacles. There is a need to screen and optimise feedstocks with higher reactivity and accessibility. Apart from that, another challenge is the economic limitation to further study and implement it. Developing a common methodology to compare potential mineralisation processes can help in assessing the economic feasibility of different projects. Research should focus on intensifying the carbonation process and scaling up operations to make the technology more viable for industrial applications. This entails striving to improve the reaction rates with minimal use of chemical reagents. Emerging techniques, including the combined exfoliation and mineralisation technique through stirred bead mills, are promising in terms of achieving higher carbonation yields and facilitating higher processing capacities. The prospect of substitution of fossil-based carbon by carbon from sustainable biomass in mineral processing industries upholds more investigation, as the transition can effectively reduce GHG emissions and enable a sustainable bio-carbon economy. Further research into the chemistry of magnesia cement as well as the preparation of high-value products, that is, flame-retardant mineral fillers, is also crucial to offset mining and feedstock costs. Ultimately, the development of detailed and realistic techno-economic analysis tools will be essential in evaluating diverse mineralisation practices and facilitating sound decision-making on their adoption. Carbon mineralisation has great potential as a long-term way to reduce CO_2 emissions in the mineral processing sector while facilitating the creation of minerals with the added value. However, a number of obstacles must be overcome before it can reach its full potential, including as energy-intensive procedures, economic viability, scalability, and environmental trade-offs. To increase productivity and cut expenses, developments in process optimisation, the use of renewable energy, and the creation of novel catalysts and feedstocks are essential. In order to overcome technical and regulatory obstacles, cooperation between business, academics, and legislators will be essential. To ensure its sustainability and long-term influence on mitigating climate change, a comprehensive strategy that incorporates carbon mineralisation with life cycle evaluations and circular economy principles will be crucial going forward.

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Section 3

Climate Change Related Applications

Chapter 6

Dissolution and Characterization Techniques of High-Value Base Metals from Various Mineral Ore Matrices: Realization for Energy Application

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Abstract

Value-added base metals such as copper, nickel, lithium, and manganese are critical for energy applications due to their intriguing properties for catalytic and other modern energy applications. These materials play a significant role in energy storage and energy conversion, including supercapacitors, batteries, and fuel cells. The efficient separation, extraction, and analysis of metals from mineral ores is crucial for meeting the exponential growth demands for sustainable renewable energy solutions. This chapter explores the various dissolution approaches to recover these metals from complex mineral ore matrices. Additionally, the main focus of this chapter will be on acid digestion, the alkaline fusion dissolution method combined with classical chemistry, and advanced spectroscopic techniques that ensure the effective utilization of value-added base metals. This chapter will also provide an in-depth discussion of the mineralogical analysis for the mineral association of these metals using analytical characterization such as scanning electron microscopy (SEM), X-ray diffraction, petrographic microscope, and mineral liberation analysis (MLA). Furthermore, this chapter also discusses the economic viability of value-added base metals, policies and strategies for commercialization, and future gaps of critical minerals in energy conversion development and water purification. High-value base metals are crucial for energy applications, battery technologies, catalysts, and renewable infrastructure. Research and technological advancements indicate that they can bridge the gap between mineral characterization and energy sustainability, ensuring a sustainable materials supply.

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Keywords: high-value base metals, dissolution techniques, mineral characterization, complex mineral matric, energy conversion

1. Introduction

As the global energy crisis grows, environmental degradation and resource limitations caused by fossil fuel consumption have become more serious. This highlights the urgent need for sustainable energy solutions, such as renewable energy sources and advanced energy storage technologies, to mitigate environmental impacts and ensure long-term energy security [1]. Metals such as copper (Cu), nickel (Ni), lithium (Li), and manganese (Mn) are considered value-added base metals because of their critical roles in energy applications, especially in catalysis, battery technology, and renewable energy systems. Due to their unique chemical, electronic, and structural properties, they have fulfilled various roles in the modern energy sector. Battery technology as an energy storage solution enables convenient access to a wide range of portable devices, including mobile phones, laptops, and electric tools. Its advancement has significantly improved efficiency, longevity, and sustainability, making it a crucial component in modern electronics and renewable energy systems.

Most mined ores require processing before they can be transformed into usable metals or final mineral products. This involves various physical and chemical techniques to extract valuable minerals while minimizing impurities. The selection of processing methods depends on factors such as ore composition, mineralogy, and economic feasibility. The treatment of ores using physical or chemical methods is known as mineral processing. Typically, mineral processing refers to physical methods such as crushing, grinding, and separation, while chemical methods, including leaching and smelting, fall under the domain of extractive metallurgy [2]. Ores are naturally heterogeneous and unique, meaning that a single element can be found in various compounds or minerals with distinctly different compositions. There is significant variation in mineral composition within an ore body and between different ore bodies. This variability affects the selection of processing techniques, extraction efficiency, and overall economic viability. Understanding these differences is crucial for optimizing mineral recovery and ensuring sustainable resource utilization. For the purpose of mineral processing, an ore is typically considered to consist of valuable minerals and gangue (waste) minerals, which are closely associated with each other within the deposit. The separation of these components is essential to maximize the recovery of valuable minerals while minimizing the processing of unwanted materials [3]. Effective mineral processing techniques rely on understanding the physical and chemical properties of both valuable and gangue minerals to achieve efficient separation and extraction. This variation makes the processing of ores a complex and customized process depending on the specific characteristics of the deposit [4]. Ores can be classified as simple or complex based on how easily the minerals can be liberated and processed. The selection of an appropriate processing method and its efficiency are heavily dependent on the mineralogy of the ore [5]. This includes the specific minerals present, their relative proportions, composition, and the way these minerals physically occur, such as their size and the extent to which they are liberated from the surrounding material. The more complex the ore, the more challenging and specialized the processing techniques will need to be to extract the valuable minerals efficiently [6].

Since mineralogy is an extremely important aspect of the operation of the mill, it is crucial at all times to retain a thorough understanding of mineralogy so that the daily operations can be monitored efficiently. While the chemical composition of the ore may remain relatively stable, the mineralogy can change significantly. These changes can affect the processing and recovery of valuable minerals, requiring operators to adjust processing techniques and optimize mill operations to account for variations in mineral content [7]. This highlights the importance of continuous monitoring and analysis of mineralogical properties to ensure efficient and accurate analyte quantification and mineral processing. Comprehending the methodologies encompassing X-ray fluorescence (XRF), X-ray diffraction (XRD), and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SED EDS) is of paramount importance in the domain of mineral processing, as it facilitates the identification of economically significant minerals and gangue while enhancing the recovery rates of ore [8]. The selection of leaching techniques is highly dependent on ore mineralogy, environmental impact, and economic viability. Advances in acid digestion, alkali fusion, coldblock™ digestion, and microwave-assisted acid digestion methods not only promote sustainable metal extraction but also enhance instrumental analysis using spectroscopy techniques for better process control and metal recovery optimization.

1.1 Dissolution of complex ore matrices

The dissolution of complex geological ore matrices is critical for accurate elemental analysis, with various methods employed to break down geological materials into soluble forms. Traditional methods, such as acid digestion and fusion, have evolved to improve efficiency and minimize elemental loss. Fusion techniques, using fluxes like lithium metaborate ($LiBO_2$) or sodium peroxide (Na_2O_2), ensure complete dissolution but pose challenges such as high total dissolved solids (TDS) and contamination risks, which are not favorable for ICP-MS analysis [9, 10]. Acid digestion, conducted in open or closed systems, involves mineral acids like HCl, HNO_3, HF, and $HClO_4$, with hydrofluoric acid playing a key role in decomposing silicate minerals. However, challenges like the loss of volatile elements and incomplete dissolution of refractory minerals persist, necessitating additional treatments like alkali fusion or ultrasonication. The general operating principles of the aforementioned methods are summarized in the schematic illustrated in **Figure 1**. Recent advancements focus on improving dissolution efficiency while mitigating health and safety concerns associated with aggressive acids like HF. Alternative techniques include Coldblock™ digestion, which allows rapid sample breakdown under controlled conditions, and microwave-assisted acid digestion, which enhances dissolution rates and accuracy, particularly for refractory materials [11]. Ammonium bifluoride (NH_4HF_2) digestion has emerged as a safer alternative to HF, reducing the risk of insoluble fluoride formation. Other emerging methods, such as laser-driven hydrothermal processing (LDHP) and X-ray microcomputer-based tomography, offer potential improvements in dissolution and analysis. Selecting the appropriate method depends on factors like sample composition, required precision, economic feasibility, and safety considerations. For clarity, [12] **Table 1** summarizes the fusion methods and digesting methods with brief descriptions, providing a thorough comparison of their key principles, benefits, advantages, and disadvantages.

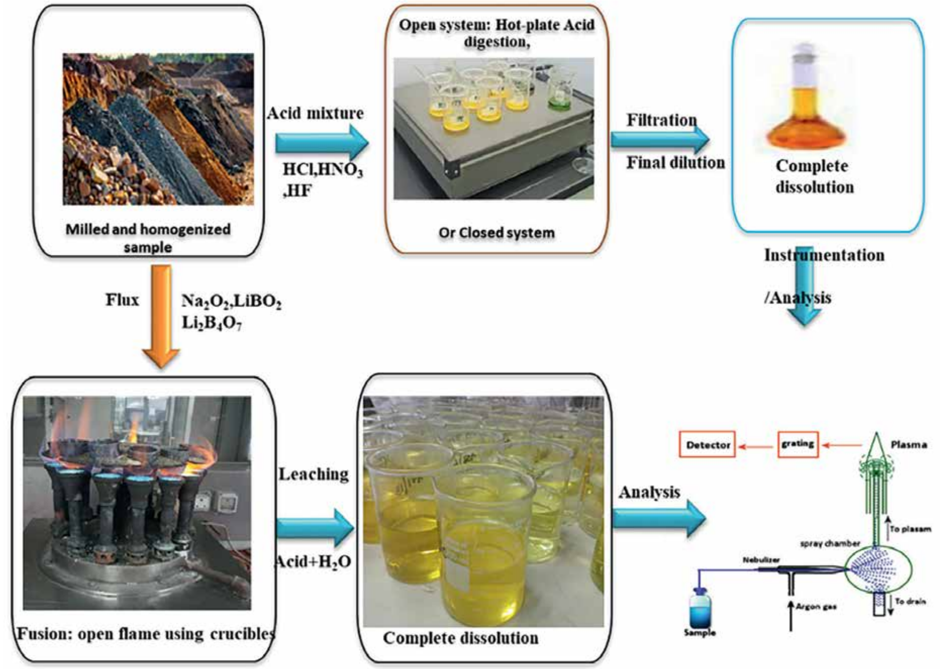

Figure 1.
Schematic illustration of dissolution methods for geological samples, fusion, and acid digestion.

1.2 Factors to consider for the dissolution process in complex geological ore matrices

The dissolution process of geological samples in complex matrices is influenced by various factors, including sample composition, environmental conditions, and the chosen dissolution method. Understanding these factors is crucial for accurate analysis and characterization of geological materials.

Factors to consider for the dissolution method and evaluation of various dissolution techniques are vital for the accurate and precise determination of elemental concentration. These factors comprised (i) sample composition (i.e., the presence of mineral or type of rock and (ii) environmental and structural factors (i.e., CO_2 injection alters pores and fracture features). For example, sodium peroxide is a strong alkali flux oxidizer, which provides rapid decomposition of the silicates, zircon, tourmaline, monazites, cassiterites, and chromites. Fusion or sintering with sodium peroxide is generally applied with the sample to a flux ratio of 1:4 at a temperature of 480°C ± 20°C for 30 minutes in a muffle furnace [22]. There is an extensive search for effective methods for complete and rapid dissolution. For example, it was taken into consideration that the recent and emerging methods, such as ammonium biflouride digestion and other digestion methods as illustrated in **Table 1**, provide high-resolution imaging of dissolution processes, revealing insights into the interactions between rocks and fluids at various sizes. Other alternatives to digestion methods for analytical techniques comprise wet chemical analysis and other classical methods, which do not require the use of instrumentation. The wet chemical analysis methods are discussed in detail in the subsections later in the chapter.

Method	**Reagents (acid, flux) and reaction conditions**	**Ref.**	**Advantages**	**Disadvantage**
Lithium metaborate Sodium peroxide	LiBO2, Li2B4O7 Na2O2, NaOH, NaCO3	[9, 10]	Dissolve silicates and refractory minerals completely Efficient for chromates, refractory, and sulfides, and ideal for ICP-OES analysis	It produces high TDS in solution, and it requires a high temperature Not good for ICP-MS due to high TDS. High Na contaminant
Ammonium bifluoride digestion	(NH4F), NH4HF2	[13, 14]	Dissolve SiO_2 minerals completely and release Ni and Cu analytes efficiently	May fail to dissolve certain sulfides or chromite minerals completely
			Reduces silica interference and compatibility with both ICP-OES and ICP-OES, which yields accurate results for trace elements	Releases toxic gas like HF
Cold block digestion	Acid mixture, HClO4, HCl at controlled heating (~ – 5°C)	[15, 16]	Reduces nickel loss by minimizing valorization Suitable for Cu in sulfides and oxides	Ni-ore with high silicate requires high temperature, which may be a challenge for colblock.
			Uniform and controlled heating for consistent Ni extraction	Ni-ore-like laterite may completely dissolve with no acid mixture
			Efficient for Li-bearing minerals such as spodumene	High sulfide minerals may be a challenge that requires additional reagents and temperature increase
Microwave-assisted acid digestion	Acid mixture, high temperature, and high pressure	[7, 11, 15–21]	Effective for Li-bearing minerals like lepidolite and spodumene and sulfide-rich Ni and Cu ores such as chalcopyrite and pentlandite The high temperature and pressure enhance dissolution efficiency.	Challenge for refractory minerals like chromite in nickel and zircon) cannot dissolve completely The high pressure and temperature require cooling before handling
Open system Closed system acid digestion	Strong acid: HNO3, HCl, HF, H_2SO_4, H_3PO_4 on hot plates High-pressure autoclave		An open system has a low-cost setup that requires simple equipment like beakers, digestion tubes, and hot plates.	Open system: Risk of loss of volatile elements such as As, Hg, and Li Ineffective for refractory minerals like silicates and oxides, and is a slower process It requires a fume hood, and it has the challenge of acid-drying There is a limited sample size (commonly less than 1 g/vessel) It may require an autoclave and a microwave, which are expensive
			It can handle larger sample sizes.	
			It can concentrate the solution easily by evaporation While closed system: It is fast to digest because of high pressure and temperature	

Table 1.
Summary of key principles of the dissolution method, advantages, and disadvantages.

2. Wet chemical analysis and other classical methods for the determination of selected mineral ores

Wet chemistry techniques have long been fundamental in the qualitative and quantitative analysis of mineral ores [23]. Effective extraction, refinement, and use in energy applications depend on the precise identification of high-value base metals from a variety of mineral ores [17]. Wet chemistry and other traditional analytical techniques are still in use because of their dependability, affordability, and capacity to examine intricate ore matrices [24]. These methods—gravimetric, titrimetric, colorimetric, and traditional spectrophotometric—offer crucial information about the composition and quality of ores like Ni, FeCr, Cu, Mn, and Li [25]. Classical wet chemistry methods remain essential for cross-validation and quality assurance of analytical data, especially in settings with limited resources, even in the face of the development of sophisticated instrumental techniques. This approach is appropriate for high-value base metals because, despite its time commitment, it yields extremely accurate and precise findings [19].

2.1 Wet chemistry techniques for ore dissolution and analysis

Wet chemistry methods for dissolving and analyzing ore include leaching, acid digestion, and traditional titrimetric or gravimetric techniques to extract and measure metal content [20]. Common acids like HCl, HNO_3, H_2SO_4, and aqua regia are used to dissolve ores, and precise metal measurement is achieved using gravimetric precipitation and complexometric titrations [e.g., ethylenediaminetetraacetic acid (EDTA) for metal ions]. Although these methods are commonly used and reasonably priced for analyzing high-value base metals, accurate control of reaction conditions and expert handling are necessary for accurate results [23]. **Figure 2** shows how wet chemistry techniques are used to characterize the chemical composition of the samples.

Titrimetric analysis, including complexometric and redox titrations, is an essential classical approach for mineral characterization [16]. For example, ethylenediaminetetraacetic acid (EDTA) titrations are employed for the detection of metal ions such as Ca, Mg, and Cu in ores, while redox titrations utilizing potassium dichromate or permanganate are excellent for analyzing iron and other transition metals [26]. These titration techniques are popular in ordinary laboratory testing for mineral processing and beneficiation because they are affordable, require little equipment, and are easy to use. Furthermore, a simple method for analyzing metal concentrations is provided by traditional colorimetric techniques, which depend on the creation of colored complexes between metal ions and particular reagents [17]. When calibrated correctly, spectrophotometric methods like the Nessler reagent for ammonia or the use of dithizone for lead and barium yield accurate findings [21].

Wet chemistry-based mineral characterization also heavily relies on separation methods, including solvent extraction and precipitation processes [13]. To help with the purification and measurement of important metals, selective precipitation, for example, can isolate particular metal hydroxides by modifying pH levels. Metal recovery from mixed ore samples can also be made more efficient by employing solvent extraction with organic ligands to selectively separate metal ions for additional analysis [14]. Despite their historical dominance, wet chemistry methods have several drawbacks, such as lengthy processes, the requirement for huge volumes of reagents,

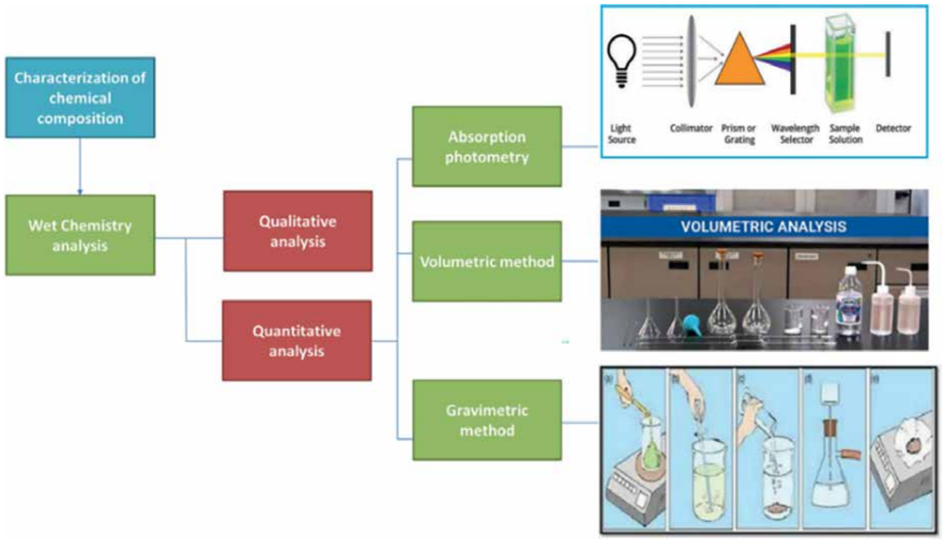

Figure 2.
Characterization of the chemical composition of samples using wet chemistry methods.

and possible environmental risks from chemical waste [24]. They are still useful, nonetheless, for cross-validation of contemporary instrumental procedures, reference standards, and situations in which advanced equipment is not available. The exact characterization of ores for energy-related applications is ensured by the combination of wet chemistry and instrumental procedures, which improves the accuracy and dependability of metal determination [27].

2.1.1 Nickel ores

Different dissolving and analytical techniques are required for nickel, which is frequently found in lateritic and sulfide ores. Nitric acid and HCl are used in acid digestion, which is followed by complexometric titration with EDTA in traditional wet chemistry procedures for nickel measurement [28]. A study on optimizing the gravimetric determination method of nickel as dimethylglyoximate for nickel raw materials was carried out by Junnila et al. [18]. The optimal pH conditions for homogeneous Ni precipitation with dimethylglyoxime were achieved when tartaric acid, stabilized by acetic acid, was added to the sample solution prior to ammonium addition. Tartaric acid proved to be successful in complexing the impurity elements. When tested using Ni concentrates and standard reference materials with high Ni concentrations, the reported optimized Ni measurement method proved to be accurate and highly reproducible [18]. A study on the comparative analysis of volumetric and gravimetric methods for the quantification of nickel (II) chloride was carried out by Ismail et al. [19]. The amount of nickel (II) chloride, as determined by the gravimetric technique, is 21.95%. In the volumetric approach, the titration of $Hg(NO_3)_2$ solution with diphenyl carbazone indicator in the sample was used to quantify the concentration of nickel(II) chloride. The volumetric approach yielded 82.64% nickel(II) chloride. Consequently, they concluded that the volumetric approach was more precise than the gravimetric approach [19].

2.1.2 Ferrochrome ores

Ferrochrome is an essential alloy in the manufacturing of stainless steel, mainly made up of iron and chromium [25]. Using oxidation-reduction titration techniques, the amount of chromium in FeCr ore is frequently determined. One popular method is to employ $KMnO_4$ or persulfate to oxidize Cr(III) to Cr(VI) and then titrate the mixture with ferrous ammonium sulfate (FAS) in an acidic medium [29]. It is also possible to determine chromium gravimetrically by precipitating it as lead chromate or chromium(III) hydroxide. Using H_2SO_4 and H_3PO_4, wet digestion techniques efficiently dissolve FeCr ores for further examination [29]. Gharti et al. [16] conducted a study on the analysis of hematite ore collected from Pokhara in Nepal. Gravimetric, titrimetric, ultraviolet visible spectrophotometry (UV–Vis) spectrophotometric, and atomic absorption spectroscopy techniques were used to do the chemical analysis. The results of titrimetric examination for the following parameters are shown in percentage areas: silica (47.06 ± 4.01), iron (36.75 ± 2.50), and loss on ignition (1.76 ± 0.17). The obtained hematite sample has an intermediate Fe level, according to the chemical analysis [16].

2.1.3 Copper ores

Wet chemistry methods like iodometric titration and gravimetric analysis are used to analyze minerals that include copper, such as $CuFeS_2$ and $Cu_2CO_3(OH)_2$. In an iodometric titration, potassium iodide is used to convert Cu(II) ions to Cu(I), and the resulting iodine is titrated with $Na_2S_2O_3$ to measure the concentration of copper [14]. For rapid copper content assessment, colorimetric techniques that create a blue copper-ammonia complex with NH_4OH are also employed. Kugeria et al. carried out research on the wet chemical approach to extracting copper [20]. This was accomplished by employing a wet chemical process that uses hydrazones made on-site from a solution leached from chicken excrement. The results of this study have demonstrated that there is a lot of potential for producing copper at a low cost, which could be used in huge enterprises as well as small-scale cottage industries using easily accessible resources like chicken dung [20].

2.1.4 Lithium ore

Titrimetric or spectrophotometric techniques are used for measurement after acid digestion in wet chemistry approaches for lithium ore analysis. Lithium is often extracted using sulfuric or hydrochloric acid and subsequently examined using ion-selective electrodes, flame photometry, or atomic absorption spectroscopy (AAS) [30]. Gravimetric determination can also be accomplished by precipitation techniques, such as the production of lithium carbonate. Although wet chemistry methods yield consistent findings, proper lithium quantification necessitates cautious handling of the reagents, lengthy processing durations, and thorough interference control [24]. A study on the quantification of lithium and mineralogical mapping in crushed ore samples using laser-induced breakdown spectroscopy was carried out by Rifai and co-workers [31]. The empirical mineral chemistry formula was used to infer the lithium concentrations, whereas the second method involved using the crushed material to construct a traditional calibration curve in order to estimate the lithium concentration in unidentified crushed materials [31].

2.1.5 Manganese ores

Oxidation-reduction titrations are necessary for the precise quantification of manganese ores, such as pyrolusite (MnO_2). Potassium permanganate volumetric manganese determination in acidic circumstances is one of the most widely used techniques [17]. Using iron(II) sulfate, the Mn(IV) in the ore is reduced to Mn(II) in this process. It is then reoxidized using a standard permanganate solution, and a persistent pink color indicates the endpoint. A solution of HCl and HNO_3 is used in wet digestion procedures to completely dissolve Mn ores prior to examination [32]. The wet chemistry techniques and other traditional methods for identifying the main elements in various mineral ores are highlighted in **Table 2**.

2.2 Classical spectroscopic and electrochemical methods

Classical spectroscopic and electrochemical methods for mineral ore determination include UV-Vis, AAS, and inductively coupled plasma optical emission spectroscopy (ICP-OES) for precise elemental analysis [19, 27]. These methods provide excellent metal measurement sensitivity and specificity. For the quick and economical detection of trace metals, electrochemical techniques like voltammetry and potentiometry are available. Electrochemical techniques are useful for real-time monitoring in mineral processing because they allow for in situ analysis, whereas spectroscopic approaches necessitate sample preparation and calibration [28]. Traditional procedures for dissolving and analyzing ore, like acid digestion and gravimetric, titrimetric, and spectroscopic approaches, provide reliable, economical, and extremely accurate results for characterizing minerals [24]. These techniques are commonly used in industrial and regulatory contexts and offer accurate quantification. They might not have the sensitivity required for trace-level detection, though, and they might be time-consuming and need dangerous reagents. Furthermore, complex matrices provide challenges for certain classical techniques, requiring sophisticated sample preparation procedures to reduce interferences and enhance analytical precision [27].

3. Advances in analytical techniques for the characterization of critical minerals from various ores

The characterization of critical minerals from various ore matrices is essential for efficient processing, extraction, and utilization in energy, electronics, and advanced material applications. The criticality of a metal is determined by various factors, including its geological abundance, potential for substitution, mining technology, and, notably, the geopolitical concentration of its supply. Recent advancements in analytical techniques have significantly enhanced the ability to accurately identify, quantify, and analyze minerals, resulting in improved recovery and processing efficiencies despite the source of supply. Over the past decade, analytical instruments have evolved from AAS (Atomic Absorption Spectroscopy), ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy), to ICP-MS (Inductively Coupled Plasma Mass Spectrometry), driven by advancements in technology and improvements in sensitivity [4].

3.1 Atomic absorption spectroscopy (AAS)

Atomic Absorption Spectroscopy (AAS) is one of the most established techniques for elemental analysis, widely used in commercial applications. Flame Atomic

Mineral ore	Primary element(s) of interest	Wet chemistry methods	Other classical methods	Reference
Nickel ores	Ni	Gravimetric precipitation (dimethylglyoxime)	Volumetric (Redox titration with EDTA)	[25]
FeCr ore	Fe, Cr	Dichromate oxidation, potassium permanganate titration	Colorimetric methods (diphenylcarbazide for Cr)	[30]
Copper ores	Cu	Iodometric titration (Cu^{2+} reduction)	Electrogravimetry, AAS	[32]
Manganese ore	Mn	Oxalic acid titration, sodium bismuthate oxidation	Spectrophotometry (Formaldoxime method)	[32]
Lithium ore	Li	Flame photometry, acid dissolution with HCl	Conductometric titration, ion-exchange methods	[31]

Table 2.
Wet chemistry techniques are used for determining major elements in different mineral ores.

Absorption Spectroscopy (FAAS) was first introduced in 1952 and became commercially popular in the 1960s due to its simplicity and reliability. This technique is employed to determine the concentration of elements in a sample by leveraging the ability of ions or atoms to absorb light at specific, characteristic wavelengths. The relationship between concentration and absorption intensity in AAS is governed by the Beer-Lambert law, which states that the amount of absorbed light is directly proportional to the concentration of the analyte. AAS measurements require initial calibration using a solution containing the metals of interest. This solution, known as the blank, establishes the baseline absorption, ensuring accurate quantification of the target elements [33]. One limitation of atomic absorption spectroscopy is its inability to simultaneously analyze multiple elements due to the need for specific light sources for each element. Additionally, it requires samples to be in a liquid form, which may necessitate complex sample preparation procedures. Furthermore, the technique has a relatively low sensitivity compared to other methods, making it less suitable for detecting extremely low concentrations of certain elements (**Table 3**).

AAS remains a highly effective technique for quantitative analysis of critical minerals such as Cu, Ni, Li, and Mn. It is widely used in mineral exploration, hydrometallurgy, and environmental monitoring. While it has some limitations (e.g.,

Type	Description	Advantages	Applications
Flame AAS (FAAS)	Uses an acetylene-air or nitrous oxide flame to atomize samples.	Fast, cost-effective, and suitable for higher concentrations.	Cu, Ni, and Mn analysis in ores and process solutions.
Graphite Furnace AAS (GFAAS)	Uses an electrically heated graphite tube for atomization.	Higher sensitivity and lower detection limits.	Trace lithium, Ni, and Mn detection in ores and brines.
Hydride Generation AAS (HG-AAS)	Converts metals into volatile hydrides for detection.	Detects ultra-trace elements like arsenic (As) or selenium (Se).	Environmental monitoring of ore leaching residues.

Table 3.
Types of AAS techniques.

single-element detection), its high sensitivity, cost-effectiveness, and reliability make it a preferred choice for many industrial applications.

3.2 Inductively coupled plasma optical emission spectroscopy (ICP-OES)

This technique involves using an inductively coupled plasma to excite atoms and ions in a sample. As these excited species return to a lower energy state, they emit light at characteristic wavelengths. By analyzing this emitted light, the elemental composition and concentration of the sample can be determined. This technique operates on the principle that ions and atoms absorb energy, leading to electron excitation. In ICP-OES, the energy source is an argon plasma at approximately 10,000 K. When the excited atoms return to their ground state, they emit light at specific wavelengths. The intensity of this emitted light is directly proportional to the number of ions or atoms undergoing the transition, aligning with the Beer-Lambert law. ICP-OES is widely used in the environmental industry for detecting and quantifying trace metals in water and soil samples. It plays a crucial role in the mining sector, where it aids in the accurate analysis of ore samples for valuable minerals [34].

ICP-OES offers high sensitivity and precision, making it ideal for detecting low concentrations of elements in complex matrices. Its ability to analyze multiple elements simultaneously greatly reduces analysis time, enhancing productivity in laboratories. Furthermore, its robust and reliable performance ensures consistent results across a wide range of applications, from environmental monitoring to quality control in manufacturing processes. Despite its many advantages, ICP-OES does have some limitations. One major limitation is its inability to detect non-metallic elements like carbon, hydrogen, and nitrogen, which require different analytical techniques. Additionally, the presence of spectral interferences from overlapping emission lines can complicate the analysis, potentially affecting the accuracy of the results [35]. Additionally, ICP-OES is a powerful, efficient technique for multi-element analysis in mineral processing, metallurgy, and energy applications, determining Cu, Ni, Li, and Mn in ores, leach solutions, and industrial products.

3.3 Inductively coupled plasma mass spectrometry (ICP-MS)

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is widely regarded for its exceptional sensitivity, capable of detecting elements at trace and ultra-trace levels, often in the parts-per-trillion (ppt) to parts-per-quadrillion (ppq) range. This technique is particularly useful in environmental analysis, geochemistry, metallurgy, and biomedical research, where precise elemental quantification is critical, as displayed in **Figure 3**. The combination of inductively coupled plasma (ICP) with a mass spectrometer allows for high-speed, multi-element analysis with minimal interference, making it a powerful tool for modern analytical laboratories [36].

One of the main advantages of ICP-MS is its ability to detect elements at very low concentrations, often down to parts per trillion. Additionally, it offers a wide dynamic range and can analyze multiple elements simultaneously with high precision and accuracy [37]. ICP-MS is one of the most powerful analytical techniques for critical mineral analysis, especially for trace metal quantification and isotopic analysis. Its high sensitivity, multi-element capabilities, and wide dynamic range make it indispensable in the analysis of complex ores, process solutions, and environmental samples. It plays a crucial role in the analysis of copper, nickel, lithium, and manganese in ores, helping to optimize mineral extraction processes, improve

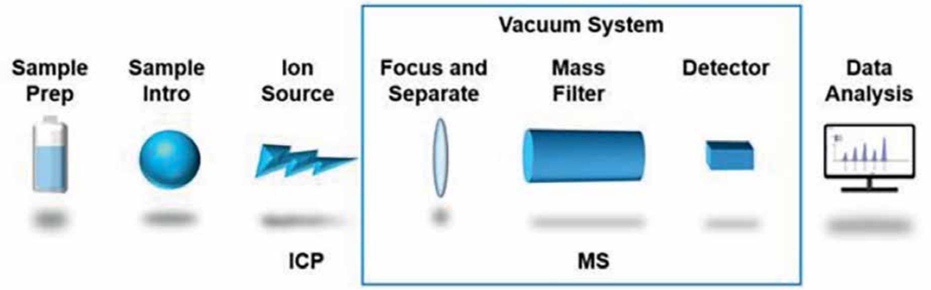

Figure 3.
Principle of ICP-MS.

product quality, and ensure sustainability in mining practices. This makes it a highly versatile and powerful tool for a variety of applications, from environmental monitoring to pharmaceutical research. Despite its many advantages, ICP-MS has some limitations. One of the primary challenges is the potential for spectral interferences, which can occur when ions of similar mass-to-charge ratios overlap, complicating the analysis. Additionally, the technique requires careful sample preparation and handling to avoid contamination, and the equipment itself can be costly to maintain and operate [27].

Due to its high sensitivity, ICP-MS is an excellent tool to be used when working with samples that do not have regulatory standard limits, since its relatively low sensitivity is most useful when dealing with samples with low regulatory standards. The ICP-MS has a greater tolerance than the ICP-OES for the amount of total dissolved solids (TDS), around 30%, making it suitable for a wider range of sample matrices. However, it has a lower tolerance for TDS (up to 0.2%) compared to ICP-OES, although various strategies, such as sample dilution, can improve this tolerance. Both ICP-MS and ICP-OES can be used for high-matrix samples, but ICP-MS typically requires sample dilution to ensure accurate results. Additionally, ICP-MS offers a broad dynamic linear range, which allows it to measure a wide range of element concentrations in a single analysis (**Table 4**) [38].

Advantages	Details
Ultra-high sensitivity	Detects elements at ppt (parts-per-trillion) levels, ideal for trace analysis.
Multi-element capability	Can detect multiple elements in a single run, making it efficient for complex samples.
Wide dynamic range	Can measure concentrations ranging from ultra-trace (ppt) to high (ppm) levels.
Isotopic analysis	Capable of performing isotopic ratio analysis, useful for geochemical and provenance studies.
Low detection limits	Ideal for detecting trace metals like lithium (Li), manganese (Mn), nickel (Ni), and copper (Cu) in ores.
Precise quantification	Provides accurate and precise quantification with minimal sample preparation.
Multi-element capability	Can detect multiple elements in a single run, making it efficient for complex samples.

Table 4.
Advantages of ICP-MS in mineral analysis.

3.4 Trends in XRF and nondestructive techniques for quantification of selective mineral ores

X-ray fluorescence (XRF) is a nondestructive geochemical analysis instrument that efficiently collects a high volume of data with multiple elements of data at a moderate value [39]. The XRF technique uses high-energy radiation to detect the unique X-rays produced by an analyte in a sample when irradiated with a beam. Since the first X-ray spectrometer was developed in the 1940s, different XRF designs and configurations have emerged. Designs vary in spectrometer size, optical route geometry, and detector modes. XRF is commonly used in analytical chemistry, geology, food and drug detection, environmental monitoring, archaeology, and other fields [40]. Almost vital features of the method are its multi-elemental nature, portability, ease of automation, speed and economy, and ability to examine solid samples without dissolution [39]. For optimal results in XRF spectrometry, the sample must be ground into a powder and then pressed or fused to form a disk [41]. The use of XRF as a common analytical method has significantly increased over the past 15 years. Environmental analysis has grown rapidly in recent decades due to the need to assess the quality of our environment using reliable data. The design of miniaturized X-ray sources, the development of low-power microfocus tubes, advanced X-ray optics, non-toxic carbon-based detector windows with higher X-ray transmittance, and improvements in signal detection systems are among the recent technological advancements that have enabled the use of XRF for low-Z element determination and the acquisition of high-resolution 2D and 3D information at the micrometer scale. Similarly, the approach of XRF for many analytical problems that can even be effectively solved in on-site or online situations has been further promoted by recent designs and commercialization of benchtop and portable instrumentation that offer extreme simplicity of operation in a low-cost design. Advancements in XRF analysis have enabled elemental analysis of natural and anthropogenic materials, leading to new analytical capabilities and numerous environmental applications.

For operational field decisions (such as exploration, mining, site remediation, or waste management), this technology offers real-time or nearly real-time decision support. It also offers an affordable substitute for traditional laboratory analysis programs and effectively handles remote or challenging field conditions [42]. Relative element abundance determination, grid mapping of a site, dynamic sampling plans based on field observations and measurements, and sample screening and selection tasks can all be successfully completed with pXRF. Portable X-ray fluorescence (pXRF) has developed from prototypes to become a crucial method for geochemical analyses in the field, particularly for environmental and mining applications. In addition to being environmentally friendly and time-efficient, pXRF was found to be a non-invasive technology that qualifies for “Green analytical chemistry” status and living material research [42]. A pXRF is used in waste management and remediation to confirm waste loads prior to disposal or treatment and identify unknown waste composition [42]. Although field portable XRF (pXRF) instruments have been around for more than 20 years, mineral exploration has only begun to make extensive use of them in 2007. More recent models of non-radioactive X-ray sources have reduced many of the safety and health risks connected to older pXRF technology. Although recent detector advancements have produced improved detection limits and data precision adequate to address many geological questions, they do not compare to lower detection limits from laboratory analyses for the majority of elements [43]. The purpose of the pXRF is to supplement other analytical techniques used in labs through selective sampling, not to replace them.

Currently, the most popular XRFs are energy-dispersive (EDXRF) and wavelength dispersive X-ray fluorescence (WDXRF). Nondestructive techniques such as XRF and proton induced X-ray emission spectroscopy (PIXE) spectroscopy are widely used to ascertain the composition of materials, such as solid, thin-film, and powder samples [44]. In contrast to conventional WDXRF and EDXRF techniques are known to have significantly higher detection limits and lower energy resolution. The energy-dispersive system is positioned more steps up the front of WDXRF in environmental practice due to its affordable rate, portable design, and simultaneous multi-elemental capabilities. Improvements in spot size and collimator optimization, stability, X-ray tube miniaturization, and thin window detectors have significantly increased the capabilities of EDXRF. These advancements, along with improvements in software and circuitry for stable digital pulse processing, have made it possible to analyze fundamental geochemical parameters in new ways, with lower detection limits and greater portability [45]. For more than 60 years, analysis by XRF has been widely used as a nondestructive analytical method for elemental analysis, and it is frequently mentioned as the most effective way to rapidly screen components [46]. For measurements used in the scanning process, speed and accuracy are essential, and portable analytical tools like XRF, laser-induced breakdown spectrometers (LIBS), and Raman offer these qualities. Nondestructive methods, such as optical, ultrasound, thermal imaging, and radioscopy, are becoming increasingly important in product and material development, including material characterization, production control, and module reliability testing [47]. A number of quick and nondestructive methods for gathering different types of data from drill cores and rock samples have surfaced in recent decades [48].

Portable techniques, like XRF, Raman, and LIBS, have shown in recent years that they can generate incredibly accurate data rapidly. The pXRF proves to be a great geological tool, enabling the real-time collection of geochemical data that may directly support various exploration program steps. It can be very helpful to use this tool during the geochemical prospecting phase because the samples will be evaluated by previous assays before being sent to the laboratories [49]. Some laboratories are also using laser-induced breakdown spectrometers (LIBS) instead of portable XRF to detect inorganic contaminants because portable LIBS offers good detection limits and does not require sample preparation [46]. Spectral analysis is a quantitative and qualitative analysis method for standard elements that has become one of the most widely used methods for figuring out the composition of a substance. Analysis and detection of metal elements in metal materials, geological samples, water and environmental samples, crops and food, chemicals and petroleum, medicine and biology are among its many applications [50]. A very powerful laser pulse serves as the excitation source for LIBS, a kind of atomic emission spectroscopy. Any substance, whether it be liquid, gas, or solid, can be analyzed by LIBS. The primary advantages of applying laser-induced breakdown spectroscopy (LIBS) to the study of mineral ores, soils, and other fields are high-energy excitation, simultaneous detection of multiple elements, and in situ analysis [50]. A method for observing rotational, vibrational, and other low-frequency modes in a system is called Raman spectroscopy. This method is frequently employed in chemistry to give molecules a structural fingerprint that allows for identification.

Neutron activation analysis (NAA) is an analytical technique that has been widely used over the past 60 years to determine many elements like Ni, Cu, Mn, and Fe, to name a few, at low levels in a wide range of materials, utilized in a range of environmental and geological materials to detect trace and minor elements. A highly effective quantitative and qualitative analytical method for identifying trace elements in a variety of sample types is NAA [51]. The ability to identify rocks and minerals through optical properties like cleavage, extinction, reflective color, index of refraction, and homogeneity has long been crucial. Minerals can be identified using only optical characteristics thanks to rapidly evolving recent developments like artificial intelligence (AI) techniques, particularly face recognition technology. Traditional face recognition techniques like template matching, statistical techniques, local binary mode, Gabor and scale-invariant features, principal component analysis, Laplacian feature mapping, local preserving mapping, sparse representation, and the maturity of face recognition founded on convolution neural networks are the two main stages of face recognition technology [40].

4. Mineralogical characterization and mineral association of high-value base metals from various mineral ore matrices

Mineralogical characterization and mineral association are critical components in understanding the composition, formation, and potential uses of mineral deposits. Mineralogical studies have indicated that base metal ores primarily consist of base metal sulfides, ferruginous minerals, silicate minerals, and graphite, with base metal grains often interlocked with other minerals [52]. The mineralogical and morphological characterization of low-grade lead-zinc ore revealed the presence of base metal sulfides such as galena and sphalerite, along with other minerals like pyrrhotite, quartz, mica, feldspar, and graphite [53]. Notably, iron ores categorized as massive hard ores, laminated hard ores, fine powdery ores, and blue dust ores can be utilized with minimal processing. In contrast, sub-grade ores—including flaky, friable, shaly, ochrous, powdery, lateritic, and goethite varieties—demand specialized beneficiation techniques to render them suitable for incorporation into blast furnace feeds. This distinction emphasizes the importance of tailored processing approaches to optimize resource utilization in the metallurgical field [54]. The mineral association of base metals in ores from the Talnakh deposit includes pyrrhotite, chalcopyrite, pentlandite, cubanite, and various other minerals, reflecting the complex mineral composition of the ores [55].

4.1 Mineralogical characterization

Mineralogical characterization provides valuable information on the nature and features of raw materials, directly influencing their quality assessment and potential use. It is essential for understanding ore compositions, mineral behavior in separation processes, and the characterization of mine tailings. It is also pivotal in understanding beneficiation methods, process parameters, and ore selectivity in nonferrous metallurgy, thereby directly influencing the efficiency and profitability of ore processing. Various methods—including conventional, unconventional, emerging, complementary, and advanced imaging—have been developed.

4.1.1 Conventional methods

Conventional methods, including X-ray powder diffraction (XRD) [56], scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS) [57], electron probe microanalysis (EPMA) [58], and optical microscopy (OM) [59], serve

Technique	Purpose	Application	Advantages	Limitations	Ref.
XRD	Identifies crystalline phases and provides information on the crystal structure	Widely used for phase identification, quantification, and understanding of lattice parameters	Quantitative, effective for bulk analysis	Limited for amorphous phases, fine grains	[62]
SEM-EDS	Provides detailed images of mineral surfaces and elemental composition	Used for micromorphological examinations, elemental analysis, and understanding mineral associations.	High-resolution, precise	Expensive, time-consuming	[63]
EPMA	Quantitative chemical analysis at a microscale	Essential for detailed compositional analysis of minerals	precise, quantitative elemental analyses at very small "spot" sizes	Relatively poor accuracy	[64]
OM	Visual examination of mineral samples	Initial identification, textural analysis	Reliable, quick results	Less effective for fine grains, manual	[65]

Table 5.
Conventional techniques for base metal analysis from various mineral ores.

as the fundamental techniques for the mineralogical characterization of base metals in various ore matrices. These techniques are crucial for identifying and detailing individual mineral phases, analyzing both major and trace elements, and comprehensively understanding the mineralogical composition of ores and their associated minerals. Poojari et al. used standard XRD and SEM methods to investigate iron ore base metals. The results demonstrated that combining these methods might be considered the best way to fully comprehend the properties of the ore and how it is processed [60]. Conventional and automated methods for mineral liberation were examined in different research by Tomanec et al. [61]. According to the findings, flotation concentration may benefit from the value of mineral liberation acquired across free surface area, but not gravity separation or magnetic separation, for instance. The technique used to measure and record mineral liberation determines the prediction accuracy for the behavior of a single feed ore during the concentration process. **Table 5** summarizes the applications, advantages, and drawbacks of conventional methods for base metal analysis in various ores.

4.1.2 Unconventional methods

Unconventional techniques for the mineralogical characterization of base metals in various ores are essential for addressing the increasing complexity of ore deposits. These techniques often provide higher resolution and more detailed information compared to conventional methods. These techniques include particle-induced X-ray emission (micro-PIXE), secondary ion mass spectrometry (SIMS), and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) [66, 67]. The latest

Technique	Purpose	Advantage	Limitation	Ref.
Micro-PIXE	Elemental analysis with high sensitivity	Valuable for trace elemental analysis	Less commonly used due to higher costs	[70]
SIMS	Isotopic and elemental analysis	Isotopic, high spatial resolution, and depth profiling	Static analysis limits its applicability in understanding materials' dynamic behavior in various areas	[71]
LA-ICP-MS	Elemental and isotopic analysis	Provides high sensitivity and spatial resolution for trace elements	Elemental fractionation occurs during the laser ablation process.	[72]

Table 6.
Unconventional techniques for base metal analysis from various mineral ores.

unconventional techniques for base metal mineralogical characterization include automated mineralogy, which offers rapid and routine mineralogical information, and the integration of techniques such as x-ray computed tomography (XCT) to improve output [68]. These techniques have the potential to improve process control and aid in environmental sample analysis in the mining industry [59]. However, challenges exist in data integration and quantitative analysis when integrating different techniques. While conventional methods such as optical microscopy are still used for mineralogical characterization, automated mineralogy has the advantage of providing rapid and routine mineralogical information [69]. It can be based on expensive equipment, including scanning electron microscopes (SEM) with energy-dispersive X-ray analyzers (EDX). Unconventional techniques for mineralogical characterization offer diverse capabilities tailored to specific ore types and mineralogical challenges. While they provide significant advantages in terms of resolution, sensitivity, and data richness, they also come with challenges such as high costs, complex data integration, and the need for specialized equipment. For a comprehensive overview of the purposes, advantages, and disadvantages of these unconventional methods in base metal analysis, please refer to **Table 6**.

4.1.3 Emerging, complementary, and advanced imaging techniques

Emerging techniques such as automated mineralogy (AM), X-ray computed tomography (XCT), and optical microscopy are revolutionizing the mineralogical characterization of base metals in ore samples [73]. These innovative techniques surpass conventional methods like X-ray diffraction (XRD) and scanning electron microscopy (SEM) by offering three-dimensional imaging, multi-scale analysis, and advanced mineralogical assessments. Automated mineralogy and XCT excel in providing three-dimensional insights and comprehensive analyses, effectively overcoming the limitations associated with the two-dimensional evaluations of conventional approaches [74]. Furthermore, optical microscopy serves as a reliable and swift alternative for mineralogical characterization, potentially yielding significant cost savings compared to the more expensive equipment typically employed in traditional methods [75]. The advancements offered by these emerging techniques for base metal mineralogical characterization are profound. Warlo et al. [76] highlighted the feasibility of multi-scale correlation analysis between automated mineralogy (AM) and X-ray computed tomography (XCT). Their research demonstrated that automated mineralogy could enhance the classification of XCT data, and conversely, by exploring the mineralogical characteristics of gold, bismuth minerals, scheelite, and molybdenite. Furthermore, XCT not only aids in refining subsampling strategies for heavy trace minerals intended for AM analysis, but it also provides essential three-dimensional context to the two-dimensional quantitative data generated by AM. Therefore, the integration of AM and XCT significantly elevates the effectiveness of both methodologies.

Raman spectroscopy and X-ray fluorescence (XRF) serve as complementary techniques in mineralogical characterization [77]. Raman spectroscopy is particularly adept at determining intricate molecular insights and identifying diverse mineral phases, while XRF excels in providing rapid and precise elemental analysis [78]. The combination of these two techniques can yield a holistic understanding of the mineralogical characteristics of samples. Nonetheless, challenges remain in the application of complementary techniques, especially concerning data integration and spatial interpretation. When selecting appropriate techniques, critical considerations include the need for high-resolution analysis and the capability to quantify process-relevant mineral parameters.

Advanced imaging technologies, including SEM, Optical Image Analysis (OIA), X-ray microtomography (μ-CT), and Deep Learning Algorithms (DLA), offer an array of capabilities for characterizing the mineralogy of base metal ores [79]. Each technique possesses unique strengths and limitations, and employing a combined approach is often advisable to attain the most thorough understanding of ore samples. Although optical microscopy is invaluable for preliminary assessments and larger-scale observations, electron microscopy provides superior resolution and detailed chemical and structural information, rendering it essential for an exhaustive mineralogical characterization of base metals. Martins et al. investigated the segmentation of quartz in iron ore using optical image analysis in conjunction with deep learning, addressing the challenges posed by quartz's transparency and its similarity in hue to the resin used for sample mounting [80].

4.2 Mineral association

The study of mineral associations involves understanding how different minerals coexist and interact within a deposit [81]. This can provide insights into the geological history and conditions of formation. The mineral associations of base metals can vary significantly across different types of mineral ores due to differences in geological settings, formation conditions, and associated mineral phases [53]. Types of mineral ores and their associations, such as polymetallic vein mineralization, orogenic gold mineralization, epithermal and skarn deposits, porphyry copper deposits, and sedimentary exhalative deposits (**Table 7**). The variation in mineral associations of base metals across different types of mineral ores is influenced by several factors, including geological, geochemical, and mineralogical conditions. The tectonic background, movements, and magmatic activities significantly influence the enrichment and mineralization of base metals. These factors control the source of metallogenic materials, their initial aggregation, and later migration and recombination [88]. The geochemical composition of the ore, including the presence of trace elements and impurities, plays a crucial role. For example, molybdenite from different mineral associations shows distinct trace-element compositions influenced by the presence of sub-nano to microscale impurities [89]. The identification of geochemical anomalies

Deposit type	Primary minerals	Associated minerals	Ref.
Epithermal veins	Sphalerite, Pyrite, Galena, Chalcopyrite	Fe-Mn Carbonates, Quartz, Ni-Fe ± As ± Sb Minerals	[82]
Polymetallic veins	Sphalerite, Pyrite, Galena	Li-bearing Mica, Quartz, Roquesite	[83]
Porphyry copper	Pyrite, Arsenopyrite, Sulfosalts	Au, Ag, Sb, Se, Co	[84]
Mississippi Valley-Type (MVT)	Sphalerite, Galena	Hydrocarbons, Metal-rich Black Shales	[85]
Porphyry Cu-Mo	Molybdenite, Pyrite, Chalcopyrite	Zonal Scheelite-Molybdoscheelite	[86]
Complex polymetallic	Sphalerite, Galena, Chalcopyrite	Bismutotellurides, Pyrrhotite	[87]

Table 7.
Key mineral associations in base metal ores.

and associations, such as those involving elements like Sn, Mo, Ag, and Bi, is critical for understanding mineralization processes and the spatial distribution of base metals. The presence of specific mineral phases and inclusions, such as native bismuth, galena, and anglesite, can significantly affect the mineral associations [88]. For instance, molybdenite in base metal associations is characterized by high Pb and Ag content due to abundant micro-inclusions of galena and Ag-S phases. Hydrothermal processes and multi-event mineralization can lead to variations in metal associations. For example, orogenic Au deposits with atypical metal associations show multiple successive mineralization events, leading to local variations in metal associations [52]. The temperature and composition of hydrothermal fluids influence mineral associations, as seen in the Mikheevskoe porphyry copper deposit, where base metal minerals are formed due to epithermal overprint [90]. The size distribution and mineral liberation characteristics of the ore affect the processing and recovery of base metals [60]. Variance in elemental and mineralogical composition within different particle sizes can influence the optimal route for processing and extraction [91].

4.2.1 Association indicator matrix (AIM)

This new method quantifies mineral associations and can be used to classify ore textures and analyze breakage behavior during comminution. Understanding mineral associations and textures can create traceability from mine to mill, which is essential for quality control and optimizing processing techniques [92]. Mineral associations provide valuable information for mineral exploration, helping to identify potential ore deposits and assess economic viability. Additionally, the mineral association provides the information for the selection of a solvent, which is a type of acid for the leaching process.

4.3 High-value base metal for battery application

The growth and development of lithium-ion batteries (LIBs) have witnessed substantial breakthroughs in cathode materials, with each iteration providing better performance. The first generation, based on lithium cobalt oxide (LCO), debuted in 2000, followed by lithium manganese oxide (LMO) and $LiNiMnO_2$ in 2010. The

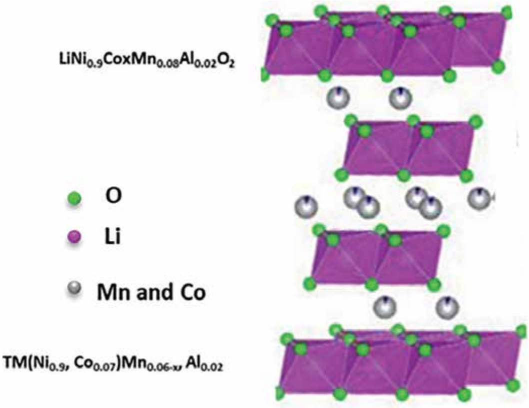

Figure 4.
Structural representation of LiNi0.9Co0.07Mn0.03O2 (NCMA) with the effects of Co and Mn on lattice stability during charge/discharge cycles.

most recent development is $LiMnPO_4$, which emerged in 2020, demonstrating better thermal stability and safety, making it a suitable contender for high-performance applications. Researchers have concentrated on improving battery performance by targeting key efficiency parameters such as high electrochemical cycling stability, a capacitance rate capability of ≥300 mAh g^{-1}, and stable operation at high voltages (cycling between 3 and 5 V), require bimetallic to give 12e- for complete oxidation, and poisoning of catalyst by alcohol intermediate. The evolution of LCO with 150–190 Wh/kg upon the incorporation of Mn improved the thermal stability (through structural integrity and lattice expansion) and safety (through reduced heat release and chemical stability). Application in bearing cathode active materials such as Ni-Co-Mn (NCM), Ni-Co-Al (NCA), Ni-Co-Mn-Al (NCMA), and Ni-Mn-O (NMO). Positive electrode materials have a significant impact on the battery's energy storage capacity. Nickel-rich nickel cobalt manganese (NCM) ($LiNi_xCo_yMn_z$, where $x + y + z = 1$) has received a lot of interest because of its high energy density, which meets or exceeds the demands of commercial-grade power batteries [93]. Zeng et al. have reported the synthetic nickel-rich NCMA, which is composed of quaternary layered oxide $LiNi_xCo_yMn_zAl_{1-x-y-z}O_2$ using the hydroxide co-precipitation method. Mn had a role in reducing the main particle size and limiting the rapid deformation of the lattice along the c-axis, whereas Co increased the value of the c-axis while decreasing the Ni^{2+} on the surface, restricting the lattice expansion along the c-axis in the voltage range of 2.7–4.3 V. **Figure 4** highlights that Mn reduces primary particle size and stabilizes the lattice, but Co affects the c-axis lattice expansion and Ni4 + ^{4+}4+ content at different voltage levels.

4.4 Application of base metal for energy conversion: Hydrogen generation

The harnessing of sustainable fuels, such as hydrogen, offers a feasible alternative to fossil fuels while addressing both the energy security and environmental concerns. Recent research has established the efficiency of nanocomposite materials, such as $CuFe_2O_4$/TCPP, in photocatalytic processes to create hydrogen from water, highlighting its potential to reduce pollution and resource depletion [94]. Due to the growing global demand for clean energy, extensive research has been conducted on energy conversion techniques, specifically water splitting, as a means of producing hydrogen. However, the hydrogen evolution reaction (HER) confronts significant problems due to high overpotentials and slow electron transfer kinetics, which reduce overall efficiency. To address these constraints, current research has looked into ways to improve HER performance, such as the development of low-cost electrocatalysts based on transition metals, including nickel (Ni), iron (Fe), manganese (Mn), and cobalt (Co). Additionally, nickel (Ni), cobalt (Co), zirconium (Zr), and manganese (Mn) are required for certain hydrogen production and storage technologies. These materials are critical in improving hydrogen technologies, but they face supply chain constraints and geopolitical concerns [95]. These materials have demonstrated improved catalytic activity and stability, making them viable options for large-scale hydrogen production. In this process, the use of Ni and Mn in electrocatalysts has shown great potential for improving hydrogen evolution reactions (HER) and overall hydrogen production. According to research, bimetallic NiMn catalysts operate exceptionally well in both alkaline and acidic conditions, making them ideal for water-splitting applications. These bimetallic materials exhibit excellent HER performance with an impressive overpotential of 1.271 V, which achieved a current density of 10 $mAcm^{-2}$. This catalytic activity is attributed to the synergistic effect between Ni and Mn, which promotes the catalytic activity promoting hydrogen production. Mn is a promoter species that enhances the hydrogen yield in many catalytic systems. The volcano plot in **Figure 5** illustrates the volcano plot for HER, indicating the current density of base metal in contrast to Platinum group metals (PGMs) such as platinum and palladium. Electrochemical catalysis of the hydrogen evolution reaction (HER) is an essential method for creating molecular hydrogen. Pt is the most effective electrocatalyst for HER due to its ability to adsorb and recombine reactive hydrogen intermediates. Nonetheless, the catalytic activity of a Pt electrode for HER in an alkaline medium is significantly lower than that in an acidic electrolyte. Extensive research has been conducted to replace platinum group metals (PGMs) in the hydrogen evolution process (HER) in alkaline media with cost-effective non-precious metal catalysts based on Ni, Co, Mn, Fe, and Mo [98]. The major goal is to create catalysts with high activity, durability, and stability comparable to or exceeding Pt while being economically viable [99].

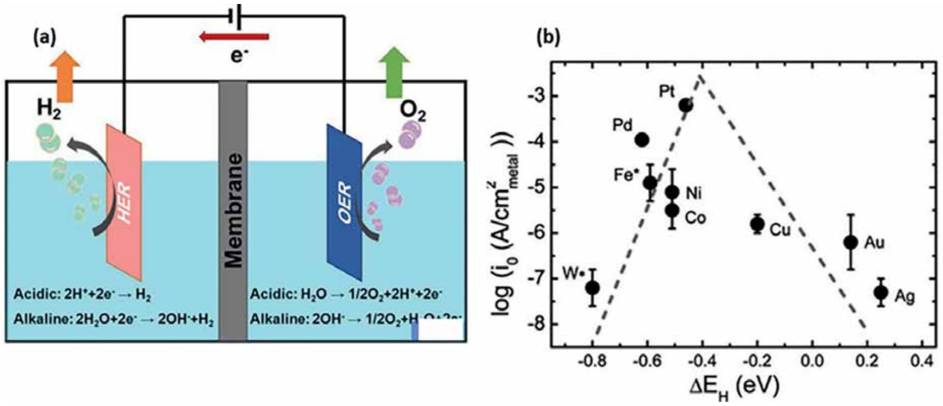

Figure 5.
(a) The water electrolysis indicating HER and (b) volcano plot for hydrogen evolution reaction in alkaline media [96, 97].

4.5 Application of base metals for water purification

Due to their distinctive characteristics, such as their high surface area, reactivity, and functionalization capabilities, bimetallic nanostructures have metallic properties emerged as a promising solution for water remediation as a vital component in modern water purification technologies, including two distinct metals, demonstrating improved characteristics for water filtration. These materials effectively eliminate pollutants owing to their synergistic effects and varied methods of action, rendering them more efficient than single-metal predecessors. These nanomaterials are a unique category of materials composed of two metals that demonstrate innovative features resulting from synergistic interaction [100]. Bimetals derived from Al (Al–Bi and Al–Sn), Mg (Mg–Pd, Mg–Cd), Ag (Ag–Pd, Ag–Pt), along with others such as Au–Pt and Ti–Fe nano-composites, can be synthesized using different technical approaches [101]. The utilization of bimetals and bimetal oxides for the removal of various pollutants from wastewater has recently attracted significant interest from researchers worldwide. The choice of metal alloy and synthesis method determines the efficacy of the pollution removal process. Moreover, the precise calibration of process parameters, such as adsorbent dosage, temperature, solution pH, contact time, and interfering anions, is vital for achieving optimal sorbent performance. Various applications, including adsorption, antibacterial, and photocatalytic properties, have been demonstrated by metallic NPs, including AgNPs, SiO_2-NPs, sulfidated nanoscale zero-valent, and persulfate treatment of NPs, as presented in **Figure 6** [103]. In water purification, these metallic nanoparticles can remove various pollutants, including heavy metals and organic compounds, achieving removal efficiencies of up to 99% in some cases. Under UV light, metal oxide nanoparticles can degrade organic pollutants, providing a dual function of contaminant removal and disinfection [104].

The high-value base metals and metallic nanoparticles offer significant advantages in water purification, but challenges such as cost and resource availability remain. Although traditional water treatment methods often struggle with emerging contaminants and may produce harmful by-products. Therefore, high-value base metals and metallic nanoparticles present innovative solutions; their integration into existing systems requires careful consideration of both efficacy and safety to address the concerns regarding their environmental impact and potential toxicity. Moreover,

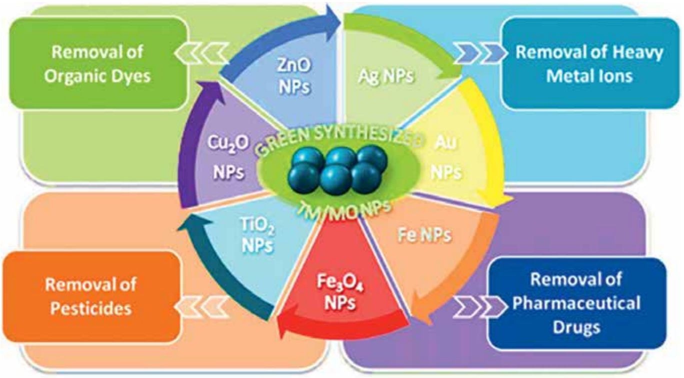

Figure 6.
Different types of metallic nanoparticles for the remediation of different pollutants [102].

comprehensive risk assessments and regulatory frameworks are essential to ensure their safe application in the real world [104].

5. Policies and strategies for commercialization

The demand for high-value base metals like Ni, FeCr, Cu, Mn, and Li in energy applications, particularly in battery technology, renewable energy infrastructure, and modern electronics, is what mostly drives their economic viability [105]. The demand for these metals has grown dramatically due to the growing global shift to renewable energy and electric vehicles (EVs), which makes their extraction and refinement profitable [31]. However, ore grade, extraction efficiency, and processing technology all affect how cost-effective production is. Advanced dissolving and characterization techniques are necessary for high-purity metal recovery from low-grade ores, guaranteeing that extraction processes continue to be economically viable while reducing waste and environmental effects [28]. The deployment of cost-effective and energy-efficient extraction methods, such as solvent extraction, hydrometallurgical processes, and bioleaching, is vital for enhancing economic feasibility. Furthermore, environmental issues underscore the need for greener production options in base metals manufacturing, addressing short-term issues with innovative inventions for long-term environmental sustainability [106]. Several mining companies are adopting ethical standards and improving mineral supply chains, but performance varies. Insufficient regulatory protections can lead to issues like weak fiscal capacity, high inequalities, and informal employment in artisanal and small-scale mining, as in the case of artisanal and small-scale mining (ASM).

In South Africa, the government has enacted the Nation Environmental Management Act (NEMA), which is a key tool in the fight to preserve and improve social norms and the environment. As supply chain management is becoming more widely recognized, international cooperation must implement appropriate standards to guarantee that trade and mineral extraction are conducted in a responsible and sustainable manner to maintain the supply of energy transition minerals uninterruptedly. Additionally, the extensive mining operations, despite superior equipment, remain susceptible to accidents resulting from equipment malfunctions and operational mistakes, highlighting the sector's persistent challenge in safeguarding worker safety. South African legislation about the mineral processing sector emphasizes safety, regulatory adherence, technological advancement, and environmental conservation [107].

The Mine Health and Safety Act (MHSA), No. 29 of 1996, mandates stringent health and safety requirements, obligating mine operators to ensure a secure working environment and to institute measures aimed at preventing accidents and fatalities. The Mineral and Petroleum Resources Development Act (MPRDA), No. 28 of 2002, regulates compliance by ensuring fair access to mineral resources, promoting sustainable development, and requiring community participation in mining initiatives. The NEMA, No. 107 of 1998, emphasizes environmental protection by establishing a framework for sustainable mining practices, while the National Water Act, No. 36 of 1998, governs the sustainable utilization and safeguarding of water resources impacted by mining activities. The Waste Act, No. 59 of 2008, requires the effective management of mine waste to reduce environmental damage. Although South African mining legislation does not explicitly require technical progress, initiatives such as the Mining Charter promote investment in innovation to improve efficiency and sustainability in the sector. Innovative processing techniques could enhance efficiency and sustainability. The environmental effects are a significant problem for the mineral processing sector. Mining operations substantially contribute to deforestation, water contamination, and greenhouse gas emissions, representing almost 10% of the world's emissions in 2018. Tailings dam failures highlight waste management risks, emphasizing immediate risk management over long-term sustainability. Addressing these issues requires a holistic strategy, including rigorous protections, sustainable technology investment, and stakeholder involvement, involving governments, industry, and local populations [107].

6. Conclusion and future outlook

The development of high-value basic metals for energy applications is critical for progressing battery technology, catalysts, and renewable energy infrastructure. Continuous research and technology improvements will help to close the gap between mineral processing and energy sustainability, resulting in a more efficient and ecologically responsible approach to metal extraction. Continued efforts in this area will be important to maintaining a consistent supply of critical minerals for the global energy transition. Moreover, the dissolution and characterization of high-value base metals from various mineral ore matrices are critical for optimizing extraction efficiency and ensuring their suitability for energy applications. This chapter has examined a number of dissolution strategies, including acid digestion, alkali digestion, and acid leaching, in addition to sophisticated characterization techniques like conventional and modern mineral composition techniques and advanced analytical techniques. By combining these methods, metal content, mineralogical relationships, and impurity levels can be precisely identified, leading to better recovery plans. Enhancing selective metal recovery, reducing reagent use, and creating environmentally friendly dissolution methods should be the main goals of future developments. By improving these methods, base metals can be used more effectively, which will help meet the increasing demand for sustainable industrial practices, energy storage, and renewable technology. The advancement of recent methods like coldblock digestion™, microwave digestion, and NH4F indicated the rapid dissolution of geological samples. Additionally, these advancements in analytical techniques for critical mineral characterization have revolutionized mineral processing by providing higher accuracy, faster analysis times, and real-time process optimization. These cutting-edge methods ensure improved recovery of Cu, Ni, Li, and Mn while supporting sustainable mining practices. Modern spectral analytical chemistry utilizes multi-element simultaneous online analysis technology to provide detailed knowledge and improve high-quality data on micro-components' internal structures in complex materials and micro-production. Improvements in X-ray fluorescence imaging are primarily driven by controversial algorithms and the need to enhance image quality. The presence of high-value base metals within diverse mineral ore matrices offers both significant challenges and remarkable opportunities for the mining industry. It is imperative to embrace advancements in processing technologies, conduct thorough geochemical analyses, and adopt sustainable practices that prioritize both efficiency and minimizing environmental impact during the extraction of these metals. Future initiatives should focus on integrating innovative techniques and comprehensive resource management strategies to ensure the long-term viability of base metal mining. Emphasis on developing and implementing sustainable mining practices to minimize environmental impact and ensure long-term resource availability. Application of mining waste and substandard raw materials as potential resources, addressing both economic and ecological challenges. Continued innovation in extraction and processing technologies to improve metal recovery rates and reduce environmental footprints. Exploration of new leaching and beneficiation techniques to handle complex and low-grade ore more efficiently. The amalgamation of machine learning with remote sensing data has emerged as a significant domain in geoscience research, enhancing precision in the identification of ore resources.

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Chapter 7

Applications of Electrochemical Techniques in the Recovery of Critical Minerals

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Abstract

The recovery of vital minerals can be achieved by electrochemical methods, which are flexible and efficient approaches to satisfy the growing demands of technological advancements and the green economy. In this chapter, the basic ideas and real-world uses of electrochemical techniques such as electrowinning, electrorefining, and electrolysis in mineral recovery are examined. Lithium, cobalt, rare earth elements, and other important minerals can be selectively recovered from ores, industrial waste, and recycled materials. The study critically examines how electrode design, electrolyte composition, and operating conditions might maximize recovery efficiency. Recent innovations like membrane-based separation, ionic liquid integration, and green energy-powered systems are highlighted for their potential to increase sustainability and reduce environmental impact. Emerging methods for overcoming these obstacles are discussed along with challenges, including energy consumption, scalability, and handling complicated matrices. This chapter highlights the importance of electrochemical methods in the circular economy and their crucial role in protecting vital mineral resources for upcoming industrial and technological breakthroughs by offering a thorough review.

Keywords: electrochemical techniques, critical minerals recovery, electrolysis, electrowinning, electrorefining, redox reactions

1. Introduction

1.1 The fundamentals and practical aspects of element extraction from ores and, eventually, other sources such as e-waste

1.1.1 Importance of critical minerals in modern industries

In the field of modern technology, key minerals are essential. They are the invisible forces that power innovative manufacturing techniques, renewable energy systems, and our digital lives. The category of minerals known as critical minerals is thought to be necessary for both national security and the economy [1]. Their extensive use across a range of industries and supply risk is what defines them. The word “critical” may not always indicate scarcity; rather, it alludes to the possible danger of a disruption in supply. This hazard may stem from geopolitical concerns, trade policy, or environmental regulations. Critical minerals are utilized in a wide array of applications, including renewable energy sources, electric vehicles, computers, and smartphones; examples are illustrated in **Figure 1** [2].

The foundation of contemporary technology is made up of critical minerals. Obstacles include globalized restricted supply, environmental concerns associated with mining, geopolitical dependencies, and inadequate recycling efforts. Supply chain vulnerabilities and environmental effects could be addressed by innovation in recycling, alternative materials, and sustainable mining techniques [3]. The foundation of technological progress and a sustainable future relies on critical minerals to promote industry-wide innovation and aid in the shift to a low-carbon economy.

1.1.2 Role of electrochemical techniques in sustainable mineral recovery

Since electrochemical techniques provide effective, selective, and eco-friendly ways to extract and refine essential minerals, they are important to sustainable mineral recovery [4]. These methods are in line with the worldwide movement to make the mining and processing sectors more sustainable. Electrochemical methods such as electrodeposition and electrowinning reduce material waste by allowing the selective extraction of specific metals from complex ores or waste streams [5]. By recovering metals such as copper, nickel, cobalt, and rare earth elements with high purity, these techniques can reduce the need for additional refinement. Talan and his colleague studied the development of recovery processes for rare earth, cobalt, lithium, and manganese from coal-based sources [6]. The purpose of this study was to create a conceptual process flowsheet for the selective recovery of several important minerals, such as cobalt, lithium, rare earth elements, and manganese, derived from coal and coal-derived materials. Nevertheless, there are still technological gaps that need to be addressed by thoroughly analyzing the techno-economics of created methods and further validating these extraction techniques, such as feedstock-specific and product-specific. Recovering valuable minerals from leachates or industrial wastewater, electrochemical processes can lower water pollution and allow for resource recyclability [7].

Critical minerals are utilized in the electronics and communication industry to make gadgets like computers and cell phones [8]. For example, high-performance

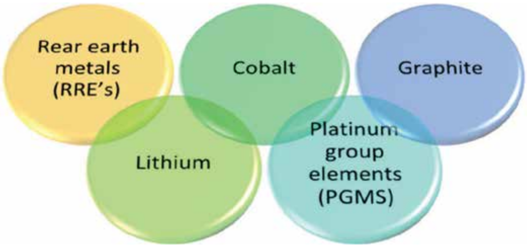

Figure 1.
Examples of critical minerals.

magnets used in speakers and hard disk drives are made from rare earth elements. Rechargeable batteries for mobile devices are made using lithium, another essential mineral in the field of renewable energy; critical minerals are important. For instance, strong magnets for wind turbines are made from the rare earth material neodymium. Lithium and cobalt are necessary for the automotive industry to produce batteries for electric vehicles [9]. Other applications include diagnostic tools and medical devices in the healthcare industry [10]. For example, pacemakers use platinum, a key material, because of its exceptional conductivity and corrosion resistance [11]. Magnetic resonance imaging (MRI) scanners and other imaging equipment use rare earth elements. Selectivity is the primary challenge [12]. Many efforts have been made to ensure selective recovery in diluted streams because the target metal ions are typically minority components in the presence of excess competing species in the primary mining or secondary waste stream. Electrochemically mediated technologies provide a desirable platform to address this selectivity issue [13].

1.1.3 Electrochemical reactions and their relevance to mineral recovery

The recycling or recovery of minerals often includes a leaching step in which the desired minerals are transferred from the solid into a solution using mineral acids, cyanide, aqua regia, and thiosulfate [14]. This, however, has major drawbacks such as high corrosiveness, volatility, toxic emissions, and low sensitivity. Therefore, the attention has been shifted to electrochemical leaching. The electrochemical leaching method is characterized as the most favorable due to its potential for energy efficiency, scalability, selectivity, and reduced impact on the environment [15]. Critical minerals such as lithium, cobalt, manganese, and REEs, which are necessary for batteries, electronics, and renewable energy technologies, can be found in abundance in e-waste, or electronic garbage. These metals may now be extracted from e-waste using efficient, economical, and ecological electrochemical recovery procedures.

1.1.4 Thermodynamics and kinetics of mineral dissolution and deposition

The manner in which the materials during the electrochemical leaching behave is governed by various laws and is also dependent on the type of material, the dissolution rate, pH, temperature, and the electrochemical potential that is applied [16]. The process follows the thermodynamic rules of converting compounds into elements; hence, a reduction reaction (Eq. (1)) would take place spontaneously if the Gibbs free energy of the reaction is negative. As an example, SiO_2 cannot be thermodynamically reduced in an aqueous solution, but it can be reduced to Si in molten $CaCl_2$.

$$M_bX_a + ae^- = bM + a/bX^{b-} \tag{1}$$

Given that there is leaching of the metals from the solid phase into the liquid phase, three typical kinetics models apply. The models include the layer mass transfer control model, the surface chemical reaction control, and the residual layer diffusion control model Eq. (2) [17]. It is widely known that in these reactions, the Arrhenius equations reflect the dependence of the rate constant on temperature, in which a higher activation energy leads to an increase in the rate of reaction, which is controlled by an increase in temperature Eq. (3).

$$f(x) = kt \tag{2}$$

$$K = Ae^{\frac{-E_a}{RT}} \tag{3}$$

Where x is the leaching efficiency, k_1, k_2, and k_3 are the slopes of the fitting lines, t is the reaction time, R is the gas constant, A is the pre-exponential factor, and E_a is the activation energy, while T is the absolute temperature [18].

The standard or reduction potential of the elements studied is crucial during the electrochemical leaching process. In most studies, it was possible to leach and separate metals such as lithium (Li) from a material consisting of cobalt (Co), nickel (Ni), and manganese (Mn), which is enabled by the difference in their reduction potentials [19]. Lithium reduction reaction has a potential of −3.0 V, while that of Co, Ni, and Mn are −0.28, −0.257, and −1.185 V, respectively [20]. Using that phenomenon, elements such as gallium and indium have been successfully separated after leaching as their potentials are far enough to enable potentiometric separation, while copper (Cu) and tellurium (Te) are often a challenge due to their potentials being in close proximity [21].

1.1.5 Mechanisms of electro-assisted leaching processes

Under electrochemical leaching, there are different techniques that operate with different mechanisms and are used for different applications. The widely known and common mechanisms are, namely, electro-sorption, electrodeposition, and electrodialysis, and they are classified as follows. Electrosorption: An electric field is applied to a solid adsorbent in order to increase its adsorption capacity. This mechanism is highly dependent on the electrode materials, such as surface area and pore size, and is often applied for the removal of heavy metals in water [22]. An electrochemical reaction is initiated, which has the capability to transform soluble and mobile metal ions into immobilized metallic coatings. Electrodialysis represents a mechanism that uses an ion exchange membrane and an electrical potential to separate the ions. In one cell, there can be an anion-exchange membrane and a cation-exchange membrane, which will then attract the right ions based on how they respond to the electrical potential applied. The perm-selectivity in electrodialysis is often affected by various factors such as membrane design, solution concentration, and electrochemical conditions [23]. Simultaneously, the solvent extraction occurs at the interface of the aqueous and organic phases to separate the Co and Li ions. It was observed that the solvent extraction process releases H^+, which then aids in the reduction leaching process, as in Eq. (4).

$$LiCoO_2 + 4H^+ + e^- \rightarrow Li^+ + Co^{2+} + 2H_2O \tag{4}$$

It was observed that using this mechanism increases the separation and recovery efficiencies by more than seven times compared to acid leaching without solvent extraction. Furthermore, the technique significantly reduced the consumption of chemicals, enhanced the utilization efficiency of protons, and simplified the recovery process. In a separate study, the leaching process was integrated with a multistage extraction process of REEs from NiMH batteries, and they observed that the recovery rate reached 90.5%, which was higher than the individual processes [24]. In order to enhance efficiency, eliminate waste, and lower energy consumption, a well-designed mineral refining process integrates several separation techniques over several phases. This is how the processing chain incorporates contemporary innovations such as pre-treatment and ore processing, primary efficiency, and separation.

1.1.6 Electrowinning and electrorefining of critical minerals

Critical minerals can be extracted, refined, and purified using the electrochemical processes of electrowinning and electrorefining. These methods are crucial for sectors that need high-purity metals for energy storage, electronics, aerospace, and other uses [25]. **Table 1** below outlines the technique comparison of electrochemical methods.

Usually, using hydrometallurgical leaching, the mineral ore is treated to create a solution with dissolved metal ions. Tunsu et al. [26] assessed the viewpoints for urban mining employing hydrometallurgical unit operations for recovering rare earth elements from end-of-life products. An electrolytic cell is used to hold the solution, and current passes directly through the solution and to the cathode. Metal ions undergo reduction and solidification. The comparison between electrowinning and electrorefining is shown in **Table 2** below [27].

1.1.7 Principles and process of electrowinning

The process of electrowinning includes reducing metal ions at the cathode of an electrolytic cell with the objective of recovering metals from solution. It is the main method for removing metal from aqueous solutions that are produced by leaching procedures. It works on the basis of the electrolytic reduction principle, which involves reducing metal ions to their metallic state and depositing them onto an electrolytic cell's cathode [28].

Method	Key applications	Advantages	Challenges
Electrowinning	Primary metal recovery	High purity, low emissions	Energy-intensive
Electrorefining	Metal purification	Extremely high purity	Requires precise controls
Electrodialysis	Ion separation	Efficient and versatile	Membrane fouling
Electrochemical leaching	Ore dissolution	Reduced chemicals, eco-friendly	Slower process
Electrodeposition	Recycling and coating	Selective recovery	Precision control needed
Electro-flotation	Fine particle separation	Low chemical use	Limited particle size range
Redox flow cells	Effluent treatment	High efficiency	Complex and costly
Galvanic coupling	Mixed-metal recovery	Simple, energy-efficient	Limited reaction control

Table 1.
The comparison of techniques of electrochemical methods.

Aspect	Electrowinning	Electrorefining
Purpose	Metal recovery from solution	Purification of impure metals
Source material	Leach solutions or industrial effluents	Impure metal anodes
Output	Solid metal deposit	Ultra-pure metal
Applications	Initial metal recovery	Refining for high-purity applications
Energy demand	Moderate to high	Moderate
Byproducts	Minimal	Valuable anode slimes

Table 2.
The comparison of electrowinning and electrorefining.

Fundamentals of electrowinning include the following:

Electrochemical reduction whereby on the cathode, metal ions (Mn+) in solution are converted to solid metal (M):

$$\mathrm{M\,n^{+} + n\,e^{-} \rightarrow M}\, mn^{+} + ne^{-} \rightarrow \mathrm{M} \tag{5}$$

The charge of the metal ion (n) is equal to the number of electrons (e −) needed.

Anodic oxidation takes place at the anode, frequently involving water or other substances:

$$H_2O \rightarrow O_2 + 4H + +4e^{-} \tag{6}$$

$$\mathrm{O \rightarrow O_2 + 4H^{+} + 4e^{-}\ H_2} \tag{7}$$

Advantages include high efficiency of metal recovery, producing metals with high purity that are appropriate for cutting-edge uses, permitting recovery from tailings, industrial waste streams, and low-grade ores [29]. Some metals, like aluminum, have a high energy need and are sensitive to electrolyte impurities that could contaminate the product or lower efficiency. Zhao et al. [30], electrochemical leaching was coupled with hydrometallurgical solvent extraction to separate and recover Li and Co from batteries. The mechanism followed is that the leaching would occur in the aqueous electrolyte for converting the solid $LiCoO_2$ to soluble ions.

1.1.8 Applications in copper, nickel, cobalt, and rare earth element recovery

A popular technique for recovering high-purity metals, including essential components like Ni, Cu, Co, and REEs. Cu, Ni, and Al have been extensively reported, while REEs, Li, Co, and Mn have not. REEs are produced via high-temperature molten salt electrowinning and are recovered from leach solutions using ionic liquid solutions [31]. High REEs purities are possible when solvent extraction and electrowinning are integrated. Neodymium, dysprosium, and praseodymium permanent magnets are used in wind turbines and electric vehicles, among other applications [32]. However, cerium and lanthanum are used as phosphors and catalysts in the electronics sector [33]. The technique makes it possible to process REEs from products that have reached the end of their useful lives in a sustainable way and reduces reliance on environmentally damaging mining operations. Electrowinning promotes urban mining, improves resource efficiency, and reduces greenhouse gas emissions [34]. Li recovery is a crucial component of rechargeable batteries, especially for energy storage systems and electric vehicles (EVs). The primary recovery method is solvent extraction (SX), this method uses ion exchange or adsorption to selectively extract lithium from brines. Direct lithium extraction (DLE) uses membranes to separate Li from solutions and precipitation (Lithium Carbonate or Lithium Hydroxide), which recovers lithium as a solid precipitate following chemical treatment and pH adjustment [35]. Applications include lithium-ion batteries for EVs, smartphones, and laptops; Grid energy storage systems; and the production of glass and ceramics [36]. Superalloys and lithium-ion batteries both require cobalt, a vital critical mineral [37]. Cobalt is extracted from Ni, Cu, and other metals in ores or battery recycling using a process called solvent extraction (SX). Cobalt is dissolved from ores or battery recycling by hydrometallurgical leaching. Cobalt is recovered as a solid material for use in battery-grade applications through precipitation (cobalt hydroxide or cobalt sulfate) [38]. Applications include cathode material for lithium-ion batteries, superalloy, aerospace industry, catalysts, and magnets [39]. In the manufacture of steel and battery applications, manganese is necessary. Manganese is extracted from leach solutions via solvent extraction (SX), particularly in nodules and battery recycling. Reductive leaching enhances manganese solubility from ores by using reducing agents (such as SO_2 and Fe^{2+}) [40]. Battery-grade manganese is recovered by precipitation using manganese dioxide or manganese sulfate. Applications include NMC cathodes in lithium-ion batteries. Alloys of steel and aluminum, and compounds used in water treatment [41]. Lithium, cobalt, manganese, and REEs are recovered primarily via hydrometallurgical procedures, specifically solvent extraction, electrowinning, and precipitation. The supply chain of vital materials required for high-performance industrial applications, battery technology, and sustainable energy must be secured using these strategies.

Industrial-scale examples	**Critical minerals**	**Reference**
Escondida Mine in Chile	Copper	[42]
Freeport-McMoRan (FCX)	Gold, silver, and molybdenum	[43]
Tenke Fungurume Mine in the Democratic Republic of the Congo	Copper and Nickel	[44]
Ravensthorpe Nickel Mine (Australia)	Nickel	[45]
Ambatovy Nickel-Cobalt Project (Madagascar)	Nickel	[46]
Glencore's Mutanda Mine in the Democratic Republic of the Congo	Copper and Cobalt	[47]
Cuba's Sherritt International	Nickel and Copper	[48]
The Chemaf Etoile Plant in the Congo		[49]
Baotou Steel Rare Earth Group	Cobalt	[48]
Lynas Rare Earths Australia	Rare earth elements (REEs) and Molybdenum	[50]
Chengdu Tianqi Lithium China	REEs	[51]

Table 3.
Industrial-scale examples and the critical mineral of interest.

1.1.9 Industrial-scale examples and efficiencies

In industrial-scale processes, electrowinning is frequently used to recover REEs, copper, nickel, cobalt, and other important metals, as seen in **Table 3** below.

Challenges in industrial operations include impurity control; solutions containing impurities may be less effective and of lower quality [52]. High energy demand, energy costs can be considerable, especially for REEs and metals like nickel [53]. REEs' scalability is constrained by their extraction and separation challenges, and requires proper control of waste and effluent is essential [54]. Renewable Energy has the potential to enhance the industrial challenges by combining solar and wind power to cut carbon emissions. Secondly, advanced electrolyte design can increase selectivity and efficiency by utilizing additives [55]. Combining solvent extraction, ion exchange, or bioleaching with electrowinning can increase recovery [56]. Electrowinning is still an important part of industrial-scale metal recovery due to the fact that it enables the sustainable production of essential materials needed for modern industries.

2. Element separation, purification, and recovery (usually, as high-value products)

2.1 Overview of key electrochemical methods

Metals and minerals can be recovered, separated, and purified using electrochemical techniques, which use electrical energy to propel chemical reactions [57]. Potentiometric, cyclic voltammetry, and chrono-amperometry are examples of electrochemical techniques [58]. As the demand for essential minerals rises and environmental concerns drive industry toward more environmentally friendly options, electrochemical techniques are becoming more and more crucial for sustainable mineral recovery. Whitworth and colleagues examined metal extraction methods that can be used to recover vital metals from mining and industry waste [59]. These methods have several benefits, particularly when combined with cutting-edge materials and renewable energy sources. The foundation of all electrochemical processes is the interplay between electrical energy and matter; the comparison of different techniques is shown in **Table 4** below [65].

2.2 Applications for lithium, vanadium, and other battery-critical minerals

Electrochemical leaching has been applied in the leaching of various critical metals, with Li being the most common, and others such as Co, Mn, Ni, Cu, and, in a minority, REEs. A majority of the studies reported a recovery greater than 90% for Li, Mn, Co, and Ni (**Table 3**). For REEs, Nd, Dy, and Pr have been leached and separated from magnets with efficiencies of approximately 98% [66]. Yang et al. [67] studied the selectivity of this technique in the extraction of Li from a lithium battery containing Ni, Co, and Mn. While the lithium recoveries at a voltage of 1.0 V were as low as the other metals, a further increase in the voltage (up to 3.0 V) saw an exponential increase in the lithium recoveries, while the impurities recoveries remained fixed. While the ability of the technique to be selective is clear, the metals can also be recovered simultaneously as illustrated by Meng et al. [68], in a novel study to leach metals from $LiNi1/3Co1/3Mn1/3O_2$ material of spent lithium-ion batteries using malic acid at

Battery items	**Cell configuration**	**Leaching agents**	**Applied voltage**	**pH**	**Leaching efficiency (%)**	**Reference**
Lithium-ion batteries (LIB)	3-electrode	H_2SO_4 Fe_SO_4	−0.3 V	>1	Li, Co, Mn, Ni: >96 Fe: >40, Cu: >70	[60]
Reduced NMC cathode	2-electrode	H_2SO_4	0.2–1.0 A		Li: 100, Ni: 90.59, Co: 90.53 Mn: 66.40	[61]
$LiCoO_2$	2-electrode	Malic acid solution	2.0–10.0 V	<6.22	Li: 94.17, Co: 90.45	[62]
Nd-Fe-B	3-electrode	$(NH_4)_2SO_4$, Na_3Cit, H_2SO_4	25–100 mA	>7.0	99.4% purity for Nd, Dy, and Pr	[63]
LIB	2-electrode	H_2SO_4	3.5 V		Li and Co: >95%	[64]

Table 4.
Application of electrochemical leaching technique for the extraction of critical elements.

a voltage of 8 V. The leaching efficiencies for the metals were between 99 and 100%. The capability of the technique to be applied to various metals indicates its versatility, thereby increasing its importance.

A good extraction method is often judged on its impact on the environment; a method producing good extraction efficiencies but endangering the environment is not favorable. Electrochemical leaching is preferred as it omits the use of corrosive acids such as hydrogen peroxide and cyanide, which are extremely dangerous. In the comparison of the typical hydrometallurgical leaching to electrochemical leaching, it was found that the latter relieved the environmental impact by 80–87% over the former [69]. In a comparison of an electrochemical leaching-solvent extraction method to pyrometallurgy, hydrometallurgy, and direct extraction, it was found that the electrochemical leaching is more favorable to the environment. Furthermore, the electrochemical method was sufficiently optimized to release lower greenhouse emissions at 2.132 kg/kg cell, which was lower than both pyrometallurgy and hydrometallurgy [70]. This further emphasizes the efficiency of electrochemical leaching, both environmentally and in terms of leaching efficiencies.

2.3 Electrodeposition techniques

One popular electrochemical method for recovering metals from complicated mixtures selectively is electrodeposition [71]. The procedure entails the controlled electrochemical reduction of metal ions from an electrolyte onto a cathode surface. Selectivity, scalability, and cost-effectiveness are some of the benefits of this extremely effective technique for recovering metals like copper, nickel, cobalt, and rare earth elements [72]. Because electrodeposition can recover high-purity metals from diluted solutions, it is a crucial technique for vital mineral recovery, especially when it comes to recycling and processing secondary resources like industrial effluents and electronic waste [73]. The selectivity of electrodeposition is one of its main advantages, and it can be adjusted by varying the electrochemical parameters, such as the electrolyte composition, applied voltage, and current density [74]. Advanced methods have been developed to improve process precision, including alternating current deposition and pulse electrodeposition. By removing some metals from multi-element solutions, these techniques reduce contamination and raise the recovered product's purity. Vanadium from industrial wastewater and lithium from brines have both been effectively recovered via selective electrodeposition [75]. Electrochemical methods for extracting metals from electronic waste are shown in **Figure 2**.

A number of case studies demonstrate the effectiveness of electrodeposition in recovering high-purity metals. For instance, Lim et al. [76] studied the use of integrated electrolyte and interface control to selectively deposit cobalt and nickel electrodeposition for recycling lithium-ion batteries. Their method is used to extract multi-component metals from electrodes made of lithium, nickel, manganese, and cobalt oxide that are purchased commercially. For cobalt and nickel, they reported ultimate purity values of 96.4 ± 3.1% and 94.1 ± 2.3%, respectively. Liu et al. [77] examined the synergistic recovery of valuable metals from spent lithium-ion and nickel-metal hydride batteries. According to their findings, the dissolution of lithium-ion batteries (LIBs) and nickel-metal hydride batteries (NiMHs) was shown to be mutually co-promoted. This led to an extraction of Li, Co, Ni, and rare earth elements (REEs) of over 98% without the need for the inclusion of any oxidants or reductants. With the addition of NaOH and Na_2SO_4 precipitants, over 97% of the REEs were recovered as an REEs-alkali double sulfate precipitate following leaching [78]. The environmental impact of conventional mining operations can be lessened by electrodeposition, which can achieve excellent selectivity and yield, according to pilot-scale research on the recovery of platinum group metals (PGMs) from mining effluents. The design and composition of the electrodes have a significant impact on electrodeposition efficiency [18]. In corrosive settings, conventional electrode materials like graphite and stainless steel may have problems, including passivation and limited endurance. Nanostructured electrodes, doped carbon-based materials, and composite coatings are examples of recent developments in electrode materials that have shown promise in addressing these issues [79]. Another important area of work is still optimizing the electrode design to maximize surface area while minimizing energy

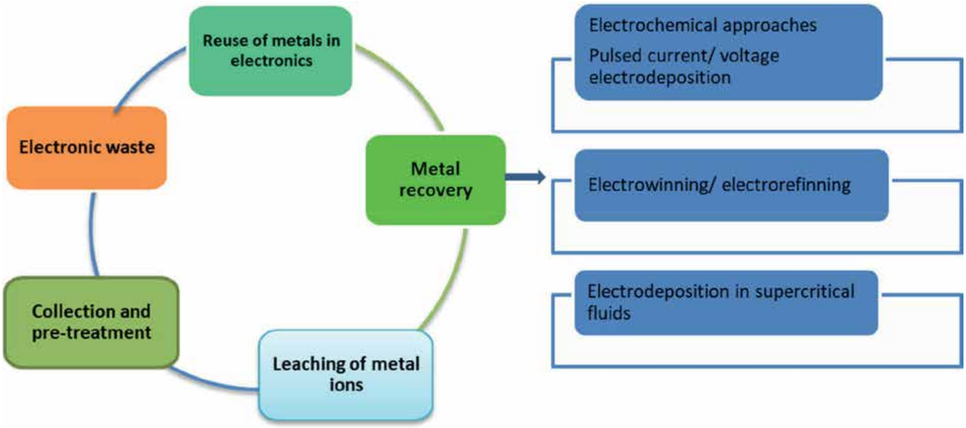

Figure 2.
Electrochemical methods for extracting metals from electronic waste.

usage. Significant technological and financial obstacles must be overcome before these cutting-edge electrode designs can be scaled up for industrial use [80].

Efficiency gains in recovery are being made possible by developments in hybrid electrodeposition techniques, such as electrochemical-membrane systems [78]. In order to improve separation prior to deposition and recover ultra-trace metals from intricate matrices, these devices incorporate ion-selective membranes. A further trend toward sustainable and energy-efficient mineral recovery is the use of renewable energy sources, like solar or wind power, to power electrodeposition operations. Recovering valuable metals from electronic waste and industrial effluents supports resource sustainability and circular economy principles. An economic argument for enterprises to use electrodeposition technology in their operations is made by the potential to recover valuable metals with little harm to the environment [81]. The demand for economical, sustainable, and effective ways to recover important minerals is driving the ongoing evolution of electrodeposition techniques. These techniques are well-positioned to contribute significantly to satisfying the expanding need for key metals across a range of industries with continued research and technological developments.

2.4 Electrochemical separation and purification

Electrical energy is used to power electrochemical separation and purification procedures, which separate or purify materials, frequently at the molecular or ionic level. Because of their effectiveness, accuracy, and environmental advantages, these techniques are frequently used in sectors like chemical manufacture, water treatment, energy storage, and medicines [82].

2.5 Ion-selective membranes and electrolytic separation processes

Ion-selective membranes are partially permeable, thin materials that let certain ions pass through while keeping others out. Cation-exchange membranes (CEMs) are one type of ion-selective membrane; positively charged ions (cations) can pass through them, composed of polymers that contain functional groups that are negatively charged, such as sulfonic acid groups [83]. Membranes that exchange ions (AEMs) are negatively charged ions (anions) that pass through polymers that contain functional groups that are positively charged, such as quaternary ammonium groups [84]. Bipolar membranes mix the layers of cation and anion exchange and encourage the dissociation of water into H^+ and OH^-, which allows for pH regulation and the production of acids and bases [85]. Applications include food processing, wastewater treatment, and desalination, which are all examples of electro-dialysis (ED) [86]. The separation of macromolecules depends on the change in surface wetness that occurs when electric stimuli are applied. In chemical engineering and environmental science, ion-selective membranes and electrolytic separation techniques are essential technologies that allow for the accurate extraction of ions and chemicals from mixtures, as seen in **Figure 3** below [87].

Research employing complicated, multi-component mixtures and long-term testing of promising devices to enable comprehensive techno-economic evaluations is noted as a widespread problem. Higher efficiencies could be achieved if the target species is given the electrical driving power that electrochemical separation devices use to directly affect separation. Su et al. [88] studied the systems for selective electrochemical separations using asymmetric Faradaics. The researcher showed that dual-functionalized asymmetric electrochemical cells are viable and perform exceptionally well. Ion-selective membranes used with electrolysis to achieve controlled separation of chlorine,

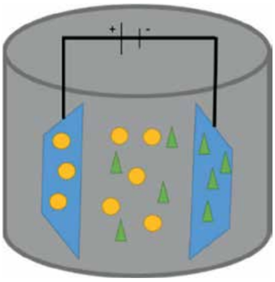

Figure 3.
Schematic diagram for the electrochemical separation process.

hydrogen, and sodium hydroxide are produced via capacitive deionization (CDI) [89]. Ion-selective membranes, such as perfluorinated polymers like Nafion, are employed in hostile environments because of their high conductivity and resilience [87]. However, hydrocarbon-based polymers are less robust but more affordable and adaptable. The addition of inorganic fillers or nanoparticles makes composite membranes for improved stability and selectivity [90]. Ion conductivity is the measure of ion transport efficiency. Secondly, the capacity to distinguish between ions with comparable charges or sizes, the capacity to withstand severe chemicals and pH fluctuations, and lastly, the capacity to withstand operational stresses and pressure [91]. One of the difficulties with ion selectivity is that impurities can obstruct membranes; high-end electrolytic membranes and systems can be costly [92].

2.6 Application in refining rare earth elements

REEs are added to steel in metallurgy to improve its strength and thermal stability. In order to increase the quantity of short hydrocarbon molecules in the final product, petroleum must be cracked using catalysts that contain a variety of REEs [93]. Compounds containing REEs are utilized in the ceramic and glass industries as coatings, polishing, coloring, decolorizing, high-temperature materials, and glass additives, as outlined in **Figure 4**. Permanent magnets, phosphors in color television tubes, x-ray tubes, fluorescent lights, electronic and computer systems, and lighter flints are the primary additional applications for REEs [94]. The addition of mischmetal or rare earth silicides for deoxidation and desulfurization is the primary use of rare earths in the steel industry. Smirnov et al. [95] reported that rare earth metals alter, inoculate, and microalloy steels and alloys. They also show a strong affinity for oxygen, sulfur, and nonferrous metal admixtures. The most significant application of REE in metallurgy is the shape management of graphite and sulfide to alter residual inclusions and hence boost steel strength.

High-purity metal compounds, such as neodymium oxides or carbonates at concentrations higher than 99%, are created by further processing REEs [96]. This usually entails separating and purifying the various REEs using methods like vacuum distillation or electrolysis.

2.7 Innovations in separation efficiency and energy use

The goals of innovations in REEs separation are to minimize environmental effects, increase efficiency, and use less energy. Recent developments in trends in technologies and element separations are outlined in **Table 5** below.

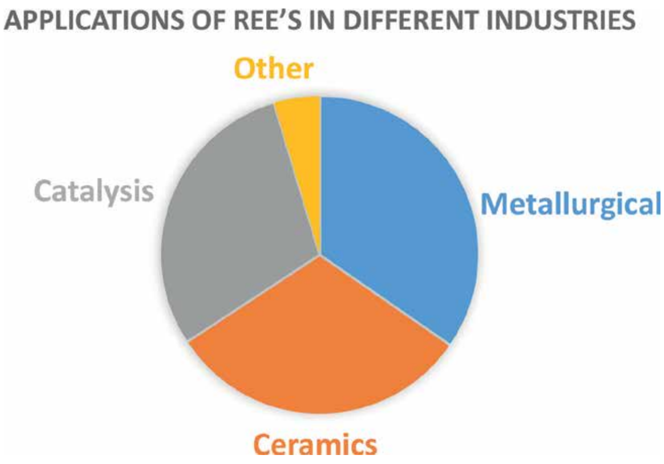

Figure 4.
Applications of REEs.

New technologies	Process	Description	Reference
Solvent extraction (SX)	Ionic liquids (ILs)	Improves selectivity and lowers toxicity by substituting conventional organic solvents, making it possible to separate REEs with greater energy efficiency.	[97]
	Continuous counter-current chromatography	Employs a liquid–liquid extraction technique that lowers the need for solvents while improving separation efficiency.	[98]
Membrane separation technology	Nanofiltration and liquid membranes	The use of liquid membranes and nanofiltration separates REEs according to ionic charge and size using selective membranes, lowers energy input, and reduces solvent consumption in comparison to conventional SX.	[99]
	Electrochemical-membrane systems	Systems with electrochemical membranes reduce processing costs by using electrochemistry and membranes to extract REEs more selectively.	[100]
Biotechnological separation (bioleaching and biosorption)	Microbial-assisted REE recovery	REEs can be extracted and bound selectively from waste materials and ores by fungi and bacteria, lessening the need for energy-intensive procedures and powerful acids.	[101]
	Peptide-based REE capture	A more environmentally friendly extraction technique is provided by engineered proteins, which bind to REEs selectively.	[7]
Electrochemical reduction and extraction	Electrochemical reduction and extraction	Extracts and refines rare earth elements (REEs) from their ores using electricity and minimizing energy consumption and the requirement for chemical reagents.	[102]
	Magnetic separation innovations	Particularly for ferromagnetic REEs, advanced superconducting magnets can increase separation efficiency.	[103]

New technologies	Process	Description	Reference
Plasma and laser-based refining	Plasma arc refining	Reduces waste by refining REEs using high-temperature plasma and has the possibility of recovering metal directly from scrap or ore.	[104]
	Laser-induced REE separation	Separates REEs according to their distinct spectra using laser excitation.	[105]
Artificial intelligence (AI) and process optimization	AI-driven solvent extraction control	Real-time SX parameter optimization by machine learning models increases yield and decreases waste.	[106]
	Computational Fluid Dynamics (CFD) in refining	Simulates and optimizes mixing, flow, and reaction kinetics to reduce energy usage.	[7]
Recycling and urban mining innovations	Electrochemical and green leaching methods	Effective REE extraction from e-waste is made possible by advancements in mild acid and electro-assisted leaching.	[107]
	Supercritical CO_2 extraction	Uses co-solvents and pressurized CO_2 to extract REEs in a low-energy, eco-friendly manner.	[108]

Table 5.
New trends in technologies for element separation.

The effects of these developments are that they can cut down on the number of processing stages to save energy. Reduced chemical waste and a smaller environmental impact, and an increased separation selectivity that boosts overall effectiveness. Lastly, increased recovery of REEs from secondary sources, such as industrial wastes and e-waste. **Table 6** outlines the costs associated with.

Ionic Solutions is working with international corporations to build the first complete industrial rare earth recycling facility in the United Kingdom. Australian start-up ElectraLith, supported by Rio Tinto, has created a direct lithium extraction (DLE) technique that improves lithium refining efficiency [109]. The technology presents a cost-effective substitute for conventional techniques and has the potential to double lithium production, much like shale does for oil. SLB (previously Schlumberger) has started a direct lithium extraction system with the goal of producing lithium for electric vehicle batteries by 2027 [110]. The system's extraction efficiency of about 90% is far higher than the conventional 50% efficiency while offering a cost-effective production. SLB has tested global brines to guarantee process resilience under various conditions and intends to replicate its oilfield services model, providing lithium extraction solutions to clients with geological reserves.

2.8 Novel electrochemical techniques

To increase recovery efficiency, hybrid electrochemical-thermal systems integrate the advantages of thermal and electrochemical techniques [111]. These systems employ thermal processes to help break down complicated mineral matrices or regenerate reagents, while electrochemical reactions are used to selectively precipitate or extract essential minerals. This synergy expands the range of resource utilization by enabling the recovery of minerals from low-grade ores and waste streams that are generally regarded as uneconomical [111]. Redox flow systems are becoming more and more

Technique	Capital cost	Operational cost	Energy consumption	Purity level	Environmental impact	Suitability for metal
Solvent Extraction (SX)	High	Moderate	Moderate	High	Chemical waste	Lithium, Cobalt, REEs
Ion Exchange (IX)	Moderate	Moderate	Moderate	High	Low	Lithium, REEs
Precipitation	Low	Low	Low	Moderate	Waste generation	Lithium, Cobalt, REEs
Bioleaching	Low	Low	Low	Moderate	Eco-friendly	REEs, Cobalt
Hydrometallurgical leaching	High	Moderate	High	High	Acid waste	Lithium, Cobalt, REEs
Novel electrochemical technique	Moderate	Low	Low	Very High	Minimal waste	Lithium, Cobalt, REEs

Table 6.
A summary table comparing associated costs with different extraction methods.

popular as a cutting-edge method of mineral recovery, especially for large-scale and energy-demanding applications [112]. These systems effectively extract and purify minerals using liquid-phase redox processes. One example is the selective extraction of vanadium from ores and industrial waste streams using vanadium redox flow batteries, which were originally employed for energy storage. Redox flow systems offer a promising way to adjust to changing ore compositions and recovery needs because of their flexibility and adaptability to changing operating conditions [113]. The efficiency and scalability of mineral recovery techniques are being completely transformed by developments in electrochemical reactor design [114]. To increase ion transfer rates, reduce energy losses, and boost selectivity, new reactor topologies are being developed, including continuous flow systems and multi-compartment designs [115]. To optimize surface area and reaction kinetics, these reactors frequently use customized geometries and cutting-edge electrode materials. For instance, by lowering fouling and improving mass transfer, reactors with alternating current fields are demonstrating promise in the recovery of rare earth elements from complicated matrices [116].

The inefficiency, excessive energy consumption, and environmental issues that plague conventional mineral recovery techniques are all addressed by these innovative electrochemical techniques taken together [117]. The circular economy and sustainable resource management are in line with their capacity to recover minerals from unusual sources, like mine tailings and industrial effluents. Additionally, their compatibility with real-time monitoring systems and flexibility with renewable energy sources make them indispensable instruments for modernizing mineral recovery operations [118]. These technologies have the potential to completely change the mineral recovery landscape as they develop further [119]. The sector is well-positioned to address the increasing need for key minerals in a way that is both economically feasible and environmentally friendly by incorporating advancements in sensor technology, hybrid processes, and reactor designs [120]. These developments represent a major step toward accomplishing global sustainability goals since they not only increase recovery efficiency but also lessen the ecological impact of mining and extraction operations. **Table 7** lists the cutting-edge methods revolutionizing electrochemical recovery procedures and demonstrates how they might be used to solve present problems in crucial mineral extraction.

2.9 Case studies and real-world applications

In the rare earth sector, electrochemical methods are being used more and more to increase productivity, decrease energy usage, and use fewer chemicals. The industrial REE refining case studies and real-world implementations of these technologies are shown below (**Table 8**).

Electrochemical methods will be essential in lowering environmental impact and enhancing REE refining efficiency due to the growing demand. Rabbani et al. [132] reported on a thorough environmental impact analysis of a novel pilot-scale method for producing rare earth oxide sustainably from coal waste. The researchers found that electricity and NaOH are the primary contributors to environmental categories that generate RE-hydroxide phases. Additionally, the synthesis stage of individual rare earth oxides (REOs), including solvent SX and precipitation processes, is greatly aided by oxalic acid, Na_2CO_3, and hydrochloric acid [133]. These programs seek to improve resource efficiency and facilitate the shift to a circular economy by certifying novel extraction and recycling techniques. Economic feasibility and process efficiency have increased significantly as a result of developments in the recovery of REEs and battery materials. Ionic

Technique	Key focus	Advantages	Challenges	Applications	Reference
Electrochemical sensors for in-situ monitoring	Real-time detection of critical mineral ions in complex matrices.	• High sensitivity and selectivity. • Real-time, on-site monitoring capabilities.	• Sensor fouling in complex samples. • Limited durability under harsh conditions.	• Monitoring mineral concentrations in leachate. • Optimizing electrochemical recovery processes.	[121]
Hybrid electrochemical-thermal processes	Combining thermal treatments with electrochemical techniques to enhance mineral extraction.	• Improved extraction efficiency. • Ability to handle refractory and low-grade ores.	• High energy requirements. • Complex system integration.	• Processing complex ores. • Recovery of critical metals like lithium and rare earth elements.	[122]
Emerging technologies: redox flow systems	Use of redox-active electrolytes for selective mineral recovery.	• Scalable and flexible design. • High selectivity for target minerals.	• High initial setup cost. • Limited electrolyte stability in some systems.	• Recovery of strategic minerals like vanadium and cobalt. • Renewable energy storage applications.	[123]
Electrochemical reactors	Advanced reactors for precise control of mineral recovery processes.	• Enhanced process control. • Suitable for continuous and automated operations.	• Requires specialized infrastructure. • Potential scaling issues in larger systems.	• Recovery of precious metals like gold and platinum. • Wastewater treatment for secondary mineral recovery.	[124]

Table 7.
Innovative techniques transforming electrochemical recovery processes.

Electrochemical method	Companies	Mineral	Reference
Molten Salt Electrolysis (MSE)	Lynas Rare Earths and China Northern Rare Earth Group	Refine praseodymium (Pr), dysprosium (Dy), and neodymium (Nd).	[125]
	Baotou Rare Earth (China)	Extract dysprosium and neodymium using 30% less energy to achieve 98–99% purity than with conventional calcium reduction [121].	[126]
Hydrometallurgical processing, electrochemical separation	REE refineries in Europe (Solvay Rare Earth Systems)	Terbium (Tb), europium (Eu), and yttrium (Y) are refined by electrochemical deposition from industrial waste and fluorescent lamp waste [122].	[127]
	Japan (Hitachi Metals)	Recover terbium and europium from phosphor powders [123].	[128]
Electrodialysis	Solvay Rare Earths (France)	Purify cerium (Ce) and lanthanum (La), 60% fewer solvent extraction steps were needed.	[127]
Magnet electrochemical REE recycling system	American Manganese Inc. (USA)	Recovered more than 90% of the neodymium and dysprosium from EV motors [124].	[129]
Plasma-assisted electrochemical	Fraunhofer Institute	Reduction of rare earths [125].	[130]
	South Korea (Korea Institute of Science and Technology, KIST)		[131]

Table 8.
Industrial applications of electrochemical techniques.

Technologies, a spin-out from the QUILL research centre at Queen's University Belfast, has created a novel method for recycling rare earth metals from used magnets using ionic liquids [110]. The method effectively yields high-purity material that can be reused by dissolving and recovering valuable components from industrial waste. In order to provide sustainable solutions to the market. These achievements show how cutting-edge technology can improve the economic feasibility and efficiency of rare earth and battery mineral recovery, resulting in a supply chain that is more self-sufficient and sustainable. A recent review by Kasri et al. [134] looked at a preliminary cost analysis of electrochemical methods, which showed economic viability when considering the cost of raw materials, reagents, operation costs, revenue, energy consumption, and net profit [135]. Their overall key findings showed a decrease in cost that is between 48 and 54% in expenses and environmental impact for electrochemical methods. If the ore recovery is high, then some of these costs, like capital costs, can be counterbalanced [135]. The ability to scale up these processes is important, hence economic feasibility is critical.

3. Conclusion

Mining, smelting, and hydrometallurgy are examples of traditional recovery methods that have been in use for many years. Conversely, alternative techniques such as electrochemical reactions, bioleaching, etc., are becoming recognized as potentially more effective and sustainable substitutes. The introduction of advanced electrode materials is revolutionizing electrochemical operations. By facilitating more efficient ion transfer and selectivity for certain minerals, these materials reduce energy consumption and boost recovery rates. In addition to guaranteeing energy efficiency, these systems satisfy the growing demand for decentralized, environmentally friendly recovery solutions. Since electrochemical methods boost economic viability, reduce environmental impact, and increase efficiency, they are crucial to the sustainable recovery of essential minerals. These methods enable the selective extraction, purification, and recycling of necessary materials with reduced energy consumption and chemical waste. Future and industry adoption prospects include growing pilot studies, AI-optimized electrochemical systems, and green hydrogen-assisted electrochemical processing, a groundbreaking method that refines metals using renewable energy. Although electrochemical approaches for recovering critical minerals have shown promise, scalability, cost, and technical difficulties remain. Innovation can increase sustainability, productivity, and economic viability by overcoming these barriers. Electrochemical methods have the potential to transform the critical minerals industry, but they must: Invest in large-scale pilot projects to show economic viability; Increase efficiency through advancements in electrode materials and electrolyte design; Develop next-generation electrode materials, like graphene and nanostructured catalysts, to improve ion selectivity and reaction efficiency. For better critical minerals separation, look at ionic liquid-based electrowinning and membrane electrodialysis. Real-time electrochemical parameter optimization using AI and machine learning models can enhance separation and energy efficiency.

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Conflicts of interest

The authors declare no conflict of interest.

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This book aims to capture the state-of-the-art of the science devoted to studying the naturally occurring inorganic materials we refer to as “minerals”, focusing on how this concept becomes crucial when developing new technologies and applications. The advent of new analytical techniques that profit from complex energy-matter interactions has provided insights into mineral structure and composition, yielding novel information about their physicochemical properties. Under specific conditions, certain minerals undergo various chemical reactions that form the foundation of mining and other human activities. There is so much richness in all the knowledge arising from theoretical and practical studies, and the different purposes minerals may be of use. Mineralogy harbours several features that are yet to be unveiled to design improved processes where minerals are the protagonists. This touches the very foundation of the major endeavors humanity is currently facing, such as green energy and other applications. This book will try to challenge readers from diverse fields of knowledge related to minerals and their associated areas. The invitation is then to dive into the latest advances in applied mineralogy to address unresolved problems where minerals have much to contribute.

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