

Extraction, Recovery, and Sintering of Manganese from Spessartine-Pyrolusite-Almandine: A Comprehensive Review

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Abstract

Manganese, a crucial industrial metal, plays an essential role in steel production, battery manufacturing, and various chemical processes, necessitating efficient and sustainable methods for its extraction and processing. The review explores the sintering of manganese extracted from these minerals, an essential step in producing high-purity manganese products for industrial use. Technological advancements and ecological considerations are emphasized throughout the review, highlighting the need for sustainable practices and green technologies in manganese extraction and processing. Economic analyses of the different extraction and recovery methods are provided, assessing their viability and scalability in global market demand. This underscores the importance of integrated approaches to manganese processing, combining traditional methods with innovative technologies to meet industrial needs while minimizing environmental impact. Future research directions and emerging technologies are identified, offering a roadmap for advancing the field of manganese extraction, recovery, and sintering.

1. Introduction

Manganese is valued for its wide use in different kinds of industrial operations. Out of all the metals, it comes in fourth place in terms of tonnage, surpassed only by iron, aluminium and copper [1]. Mainly, manganese is important in making steel stronger, tougher and more durable by acting as a key additive in the steel process. It is also needed in the production of non-ferrous alloys, batteries, chemicals and ceramics [2]. Its great contribution is to make materials tougher and more flexible which makes it essential for construction, automotive and manufacturing. Various types of manganese minerals are mined and processed and spessartine, pyrolusite and almandine are important ones [3]. Spessartine, a manganese aluminium garnet ($Mn_3Al_2(SiO_4)_3$), commonly appears in granite pegmatites and certain types of metamorphic rocks. Spessartine crystals are characterized by their rich orange-to-red-brown color, attributable to their manganese content [4]. Although it is mainly recognised as a gemstone, spessartine can also be mined for manganese when present in big amounts. The mineral pyrolusite (known as MnO_2) is the main and most abundant source of manganese ores [5]. This mineral is found in black, amorphous (without a definite form) form in sedimentary and hydrothermal environments. The manganese industry greatly depends on pyrolusite because it has a lot of manganese and also is used to produce

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ferromanganese and various chemical compounds [6]. Its capability to oxidise many substances is, therefore, very important in the glass and ceramics sectors. $\text{Fe}_3\text{Al}_2(\text{SiO}_4)_3$ is the formula for almandine, an iron aluminium garnet and it commonly has a lot of manganese. It is most commonly a reddish-brown colour and it is valued for being used as a grinding material and in gemstones. While pyrolusite provides more manganese directly, the manganese in almandine means it is also studied in manganese extraction [7]. This study lies in its comprehensive examination of the methods and processes involved in the extraction, recovery, and sintering of manganese from spessartine, pyrolusite, and almandine. The study uses information from geology, technology and the environment to guide the effective and environmentally sound use of manganese ores. By using old and new techniques together, this study hopes to fulfil industrial demands while keeping the environment safe. Many earlier studies have concentrates on certain steps of extracting and treating manganese. It also covers the full activities related to extracting, recovering and preparing manganese ore, helping to explain the whole process better. [8] tested the enhanced method of microwave-assisted carbothermal reduction on a pilot scale, revealing how it could substantially increase energy efficiency and lower consumption. Another scientific study [9] looked at how microwave calcination reduces both dissociation and thermal decomposition during the processing of manganese ore. This is a detailed analysis of the methods and procedures required to extract, recover and sinter manganese from spessartine, pyrolusite and almandine. There are three main objectives for this research: to study several mining and beneficiation practises used on manganese minerals;; to examine the sintering techniques applied to manganese and how sintering affects material properties; and to integrate geological, technological, and environmental perspectives to offer insights into the effective and sustainable utilization of manganese resources which emphasizes the importance of this research in advancing the field of manganese extraction and processing.

2. Geological and Mineralogical Characteristics

Spessartine belongs to the garnet group of minerals and has the formula $\text{Mn}_3\text{Al}_2(\text{SiO}_4)_3$. The mineral is special because it holds large amounts of manganese which creates its typical orange or brown-red colour. The shape of the crystal structure of spessartine is isometric and is part of the cubic crystal system. Inside this framework are SiO_4 tetrahedra linked by aluminium (Al) in octahedral and manganese (Mn) in dodecahedral places. Its structure is very stable and garnets can often take on different elements which changes their properties and colour. The main places to find spessartine are in granite pegmatites and specific types of metamorphic rocks [10]. Hydroxymanganate is produced under hot and pressurised conditions, often along with other manganese minerals and silicates. Unlike many other types of garnets, its presence is rare which leads to its importance as a gemstone and also as a source of manganese.

Among manganese materials, pyrolusite (MnO_2) is recognised as the most important mineral [11]. In the tetragonal system, it becomes crystallised as prismatic or acicular crystals. Edge-sharing between MnO_6 octahedra makes pyrolusite's structure both anisotropic and has layered boundaries. This arrangement gives chlorine the ability to oxidise substances and helps it be useful in many industries. Most of the time, pyrolusite is opaque, has a metallic look and leaves a dark grey or black trail. Pyrolusite is seen most often in sedimentary rocks and environments formed by hot, mineral-rich water [12]. Manganese minerals react with oxygen to form manganese dioxide or it develops as a direct precipitate from waters containing manganese. In addition to being used in industrial applications for manganese, pyrolusite is found again in smaller forms in wetlands and stream banks which results from chemical weathering processes.



Fig. 1 Structure of Spessartine

Another member of the garnet group is almandine, whose chemical formula is $\text{Fe}_3\text{Al}_2(\text{SiO}_4)_3$. There is usually some manganese in the minerals and this manganese can stand in for iron during the crystallisation process. Like spessartine, almandine is part of the isometric system and forms dodecahedral crystals [13]. The silicate tetrahedra, octahedral aluminium and dodecahedral iron (or manganese) are what the structure consists of. This specific crystal structure makes almandine both very hard and durable. Almandine often occurs in schists,

gneisses, granite and in pegmatites [14]. It crystallises when conditions are very hot and pressing, we call these conditions regional metamorphism. Spessartine, pyrolusite and almandine stand out because of their geological traits which give them value as manganese sources and make them important minerals for industry [15]. It is essential to understand the chemistry, shape and occurrence of minerals to improve ways of extracting and processing them. Understanding these concepts forms the starting point for learning about the benefits of minerals in industries, a major example being the use of manganese [16].

2.1 Extraction Processes

Out of the mining processes, surface mining is mostly used for accessing minerals available close to the Earth's surface [17]. There are numerous approaches in this method, including open-pit mining, strip mining and quarrying. At this stage, overburden (soil and rocks covering the mineral deposit) is removed to reveal the ore below. An open pit is most suitable for mining ores that are not closely clustered. Ore extraction involves drilling, setting off blasts and hauling the ore to processing plants. Strata of soil and rock are dug in order to expose where the ore is found. This method is less common for manganese but can be applied in certain geological settings, and is commonly used for minerals lying in horizontal beds close to the surface. Consequently, quarrying involves the extraction of rocks by cutting, blasting, or drilling, and is mainly used for extracting building materials, but can also be applied to certain manganese ores [18]. Underground mining is employed when ore deposits are too deep for surface mining to be viable. Techniques include room-and-pillar, cut-and-fill, and block caving.

Comminution involves reducing the size of the ore to liberate the minerals [19]. This process is critical for efficient downstream beneficiation. Large pieces of ore are crushed in stages using jaw crushers, gyratory crushers, or cone crushers to produce smaller fragments. The crushed ore is further reduced in size using mills (ball mills, rod mills, or SAG mills). Grinding produces fine particles that increase the surface area for the subsequent separation processes [20]. The extraction of manganese from spessartine, pyrolusite, and almandine involves a series of complex processes. [21] explain surface and underground mining techniques are employed depending on the depth and nature of the ore deposits. Comminution and beneficiation are critical for liberating manganese minerals and enhancing the efficiency of subsequent processes. Leaching methods, including acid, alkaline, and bioleaching, provide versatile approaches for dissolving manganese from ores. Reduction processes thermal, hydrometallurgical, and electrometallurgical—are essential for producing high-purity manganese metal. Each method has its advantages and challenges, and the choice of technique depends on the specific characteristics of the ore and the desired purity of the final product. [22] explain sustainable and efficient extraction methods are crucial for meeting the growing demand for manganese while minimizing environmental impact.

Exploring the processes for comminution and extraction with spessartine, pyrolusite and almandine has greatly increased our knowledge about these minerals and their challenges in processing. Many minerals are needed in metallurgy and the gemstone business and their proper processing helps save money and increase how much is recovered. The first important task is to reduce the ore size so the valuable minerals can be released from the rock in which they are found. The process of crushing and grinding is needed to liberate spessartine ($\text{Mn}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) and almandine ($\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) found in metamorphic rocks to prepare them for processing. Various investigations have examined the effects of ball milling, HPGRs and autogenous milling on how well particles are divided and sized. Studies found that ball milling regularly can give good results, yet this process cannot always provide even-sized particles for outstanding extraction performance. The processing from HPGR creates finer particles using less energy and this is what makes people find it a promising alternative. Work has been carried out to ensure these techniques achieve a balance between energy costs and particle reduction, as this helps improve liberation of minerals and simplifies later stages of processing. Attempts at improving efficiency in comminution and extraction persist. Sophisticated sensor and automation technology has enhanced process control and efficiency. Regular monitoring of the particle size and the minerals they bear improves circuit adjustments and leads to improved separation and recovery rates. Through improved reagent design and better structure of the process, the extraction process is effective and environmentally compatible. Ongoing research and technical development underpin addressing challenges associated with increasingly complicated ore deposits and increasingly stringent environmental regulations. Investigation of hybrid comminution technologies involving the integration of multiple crushing techniques, along with development towards less environmentally demanding approaches to extracting valuable commodities, continues. More advanced model and simulation development also assists in gaining a better understanding and optimization of comminution and extraction processes by elucidating behaviour and interaction between minerals during these processes.

2.2 Recovery of Manganese

Several methods are used to purify and upgrade manganese from ores and other secondary sources [23]. The process helps clean the manganese and provides a version with a purity that matches the needs of various industrial uses. Purification, electrolysis and recycling of scrap materials are major ways to get manganese.

Because of how efficient and selective solvent extraction is, it is often used to purify manganese as shown in figure 2.

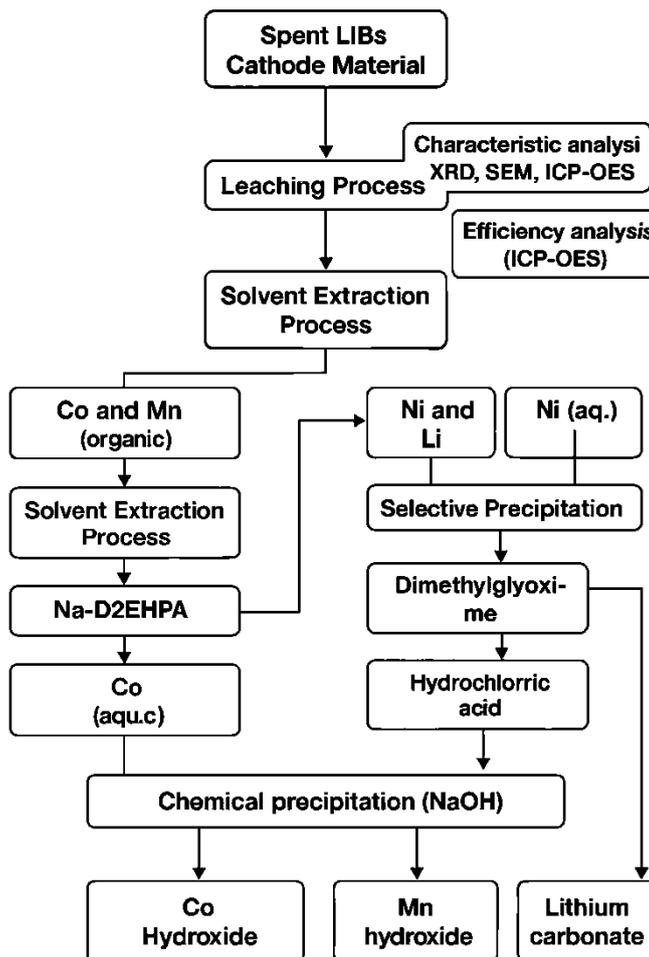


Fig. 2 Solvent extraction for the purification of manganese

It requires manganese to be taken from an aqueous solution and transferred to an organic solvent. An organic solvent is mixed with the aqueous solution that contains manganese ions to selectively part the manganese. After that, the organic phase including the manganese is divided from the aqueous phase. Afterward, manganese is then stripped from the organic solvent with an appropriate reagent, thereby reconditioning the solvent for reuse [24]. Very high selectivity and efficiency for manganese separation from impurities, ability to handle large volume of solution, and amenability to continuous operation. Need for expensive organic solvents, potential environmental hazards by solvent use, and challenge in phase separation operations. Ion exchange is another useful purification process for manganese, which is quite effective for the removal of trace impurities. The solution containing manganese is allowed to pass through a column packed with ion exchange resin. Only manganese ions get caught in the resin and the others are not blocked. A suitable regeneration chemical is used to remove the manganese from the resin. Recovered manganese is very pure, ion exchange resins are precise in choosing which ions to remove and operations are straightforward and automation is available [25]. Problems include the fact that the ion exchange resins can be very expensive, that they become contaminated or destroyed and that they need to be recharged occasionally. In precipitation, manganese is cleaned by turning insoluble compounds into small pieces that can be removed. Precipitation of manganese occurs by changing the solution’s pH or by using reagents that cause it to form insoluble compounds. Usually, sodium hydroxide, ammonium carbonate and sulphur dioxide are among the main factors that trigger precipitation. Following production, the precipitate is subjected to the steps of filtration, washing and being transformed into the final manganese material. The process is renowned for its simplicity and low cost, capacity to process large quantities of solution, and efficient elimination of certain impurities. The possibility of incomplete precipitation, production of large amounts of sludge, and necessary careful control of process parameters to prevent co-precipitation of impurities are of the utmost importance [26].

Hydrometallurgical processes, especially acid leaching, have been extensively researched for manganese recovery.

There has been research aimed at optimizing leaching conditions with sulfuric acid and other reagents. Empirical investigations showed that leaching of manganese from ores and residues with sulfuric acid is feasible, and some researchers have investigated parameters like acid concentration, temperature, and leaching time. Some investigations, for instance, have reported high recovery percentages by optimizing these parameters; however, the process tends to produce quantities of acidic waste, which is environmentally costly. Although hydrometallurgical processes have proven to be effective in enhancing manganese recovery, most past studies ignore the environmental factors associated with acid consumption and waste generation. Comprehensive studies on recycling and treatment of spent leach solutions are also lacking. This affirms that further research has to be directed into more sustainable hydrometallurgical processes, including the utilization of less harmful reagents or closed-circuit systems with the aim of wastes elimination.

Pyrometallurgical operations such as roasting and smelting have also been investigated for manganese recovery. Investigations in this field have aimed at developing optimum furnace conditions and flux mixtures to recover manganese from concentrates and ores. Although pyrometallurgical treatment can be carried out at high recovery efficiencies, it demands high energy inputs and results in large greenhouse gas emissions. Critique of pyrometallurgical research cites the energy-intensive nature of the processes and the environmental impact as major flaws. Whereas some research has been conducted into the use of alternative fuel or energy sources that are intended to reduce emissions, more research needs to be conducted to determine more energy-conserving and eco-friendly pyrometallurgical processes. Additionally, there is a lack of research into the marriage of pyrometallurgical operations and hydrometallurgical methods to enhance final recovery and sustainability.

Current studies have also investigated biological and new extraction techniques, such as solvent extraction and bioleaching. Bioleaching, which involves using microorganisms for the dissolution of manganese, has been promising in the processing of low-grade ores and tailings. Results from the laboratory demonstrate that several sulphur-reducing bacteria are able to extract an efficient amount of manganese in controlled situations. Scaling and maintaining consistency are the main problems that scientists find in bioleaching studies. Small studies in the laboratory have results, but it's been challenging to achieve the same outcomes on an industrial scale. Further studies have to be done to determine the long-term viability and effectiveness of bioleaching systems compared to conventional mining techniques.

Solvent extraction has been investigated as a process for manganese recovery from leachate solutions. This research has involved searching for some solvents and optimization of extraction conditions. Although solvent extraction is very selective and recovery efficient, the economic analysis is not complete in previous studies and environmental costs related to the use and disposal of solvents are not considered. Despite the numerous developments attained in manganese extraction in the past research, there are still some elements that need to be investigated further. The impact of mining operations on the environment is still important today, encouraging research into developing environmentally responsible technology.

Complete economic analyses are also needed to ascertain the viability of new methods at the industrial level. Future studies must emphasize the application of novel and conventional techniques for achieving the highest efficiency in recovery and sustainability. Developing improved reagents, finding the right conditions for exploitation and using environmentally friendly technologies are essential for boosting manganese recovery processes. Combining materials science, environmental engineering and industrial methods for research could bring up new solutions for manganese extraction and recovery.

Electrolytic processes such as electrorefining and electrowinning are used to obtain pure manganese through the passage of electric current in an aqueous manganese solution [27]. During electrolysis, impure manganese metal is placed as the anode, and pure manganese is deposited on the cathode. Manganese sulfate and sulfuric acid form the usual electrolyte. Impurities in raw manganese either stay in the anode slime or dissolve in the electrolyte and are unable to deposit on the cathode. The objectives are the production of manganese of very high purity, effective elimination of impurities, and the possibility of continuous process flexibility. The high consumption of energy, need for more operation equipment and control systems, and production of waste anode slimes necessitate additional processing [28]. Manganese ions in the solution are reduced at the cathode to form metallic manganese, and oxygen is evolved at the anode. The electrolyte is usually manganese sulfate in sulfuric acid solution. The process is characterized by high purity of the generated manganese, ease of operation, and the possibility to directly extract manganese from secondary materials or low-grade ores [29]. Higher electrical energy consumption, requirement of continuous monitoring and control of electrolytic conditions, and possible complications because of electrode passivation.

By taking away spent minerals and avoiding damage on the environment, manganese recycling results in improved resource use [30]. Manganese is retrieved from used steel and spent batteries and is more lucrative now compared to before. Scrap is gathered, sorted, and processed so that manganese recycling becomes achievable. Mechanical separation, hydrometallurgical processes, and pyrometallurgical operations are used to accomplish this. For instance, steelmaking slag can be processed to recycle manganese, and spent batteries can be leached

and electrolyzed to facilitate manganese extraction. Conservation of natural resources, reduction of waste and landfilling, and less energy demanding compared to primary extraction [31]. Uncertainty of scrap composition, potential contamination with toxic substances, and the requirement for efficient collection and processing infrastructure. Manganese recovery and recycling need to be environmentally benign to satisfy the sustainable criteria. The management of process by-products like sludge, leach residues, and effluents is most challenging. The environment and health can be protected from pollution through proper treatment and disposal of such by-products. The energy efficiency of the recovery processes must be enhanced to reduce the carbon footprint. Energy-efficient technologies in conjunction with renewable energy can effectively reduce environmental effects [32]. Maximization of resource utilization, for example, reagents and water, renders the manganese recovery activities sustainable. Recycling and reuse of input materials wherever feasible minimize resource depletion [33].

Manganese extraction involves a series of advanced methodologies that are designed to yield high-purity manganese for industrial applications. Various purification methods, including solvent extraction, ion exchange, and precipitation, are effective in removing impurities from manganese solutions [34]. Electrolytic recovery techniques, including electrorefining and electrowinning, also yield high-purity manganese via carefully controlled electrolysis processes. Recycling of manganese from alternative sources, including recyclable waste and exhausted batteries, is a key aspect of facilitating sustainable resource management and minimizing environmental effects. Waste management, energy efficiency, and resource effectiveness are essential considerations in the development of sustainable processes in manganese recovery [35]. With the demand for manganese persistently increasing, the development of such recovery technologies and their incorporation into the circular economy will be essential to sustain industrial requirements at lower environmental expenses.

Table 1 Summary of critical parameters for recovering manganese [37-43]

Extraction Method	Critical Parameters	Description
Hydrometallurgical	Acid Concentration	Concentration of sulfuric acid or other reagents in the leach solution. Higher concentrations can increase manganese solubility but may also raise costs and environmental concerns.
	Temperature	Operating temperature during leaching. Higher temperatures generally increase the rate of manganese dissolution but also energy consumption.
	Leaching Time	Duration of the leaching process. Extended leaching times can improve manganese recovery but may increase processing costs.
	pH Level	pH of the leach solution, influencing the solubility of manganese and the efficiency of the extraction process.
	Oxidizing Agent Usage	Incorporating oxidants like H_2O_2 or $KMnO_4$ can enhance manganese dissolution by converting $Mn(II)$ to more soluble forms.
	Solid-to-Liquid Ratio	The pulp density significantly affects leaching kinetics and reagent consumption. Lower ratios favour dissolution but require more reagents.
Pyrometallurgical	Furnace Temperature	Temperature in the smelting or roasting furnace. Optimal temperatures are crucial for efficient manganese reduction but require significant energy.
	Flux Composition	Type and amount of flux used in the process. Proper flux composition helps to facilitate manganese extraction and improve process efficiency.
	Reductant Type	Type and amount of reducing agents. Influences the efficiency of manganese reduction from ore.
	Energy Input	The total energy required for the pyrometallurgical process. Higher energy inputs can increase costs and environmental impacts.
	Atmosphere Control	Reducing or inert gas atmosphere affects manganese volatilization and impurity removal.
	Calcination (Ore Pretreatment)	Pre-roasting to remove moisture and improve reactivity prior to smelting.

Biological	Microorganism Selection	Choice of microorganisms for bioleaching. Specific bacteria can effectively solubilize manganese from these minerals.
	Optimal Temperature and pH	Conditions for microbial activity. Essential for maximizing the efficiency of bioleaching.
	Leaching Duration	The process for microorganisms to pull manganese from ores requires time. Using longer periods for training can improve the ability to recover, yet it might slow down scaling.
	Nutrient Supply	Access to nutrients for the development of microorganisms. It is important to feed microbial cultures enough nutrients for them to work and for manganese recovery.
	Microbial Consortium Use	Mixed cultures may outperform single strains due to synergistic effects in bioleaching.
	Bioreactor Design	Reactor configurations influence oxygen transfer and microbial activity.

2.2.1 Mechanistic Analysis of the Extraction of High-Purity Manganese

The process of recovery of high-purity manganese includes a series of significant steps, such as mining, beneficiation, leaching, and purification. All the operations are optimized for maximum recovery and purity of manganese with least environmental disturbance. The discursive detail on the most significant processes involved:

- i. Mining and Beneficiation: Extraction starts with mining, where manganese-bearing ores like spessartine, pyrolusite, and almandine are extracted through surface as well as underground mining [17]. Such a mined ore is comminuted, i.e., crushed and ground to shatter gangue and free manganese minerals [19].
- ii. Leaching occurs after a small amount of liberation, in which chemicals are used to breakdown and dissolve manganese from the ore. Most often, acid leaching is used which dissolves manganese from the ore with sulfuric acid [5]. Leaching can be depicted as the following reaction: $MnO_2 + H_2SO_4 \rightarrow MnSO_4 + H_2O$.
- iii. Purification: The purification of leach solution with dissolved manganese is carried out to eliminate impurities. Purification is carried out using several processes, such as solvent extraction, ion exchange, and precipitation [24]. In Solvent Extraction, Manganese ions are pulled out of water by an organic liquid that selects them. For the recovery of manganese, the solvent is stripped and high-purity manganese is created [25]. Ion exchange: Cleaning fluid pushes through the ion exchange resin, where it helps to remove manganese from the solution. Select reagents cause the manganese to be removed from the resin [26]. Precipitation: Removing manganese from the leach solution can be done by either changing the pH or including a special chemical solution. The precipitate goes through filtering, washing and drying to get manganese that is very pure [27].
- iv. Electrolytic Recovery: In the final step, electrolytic methods such as electrowinning and electrorefining are employed to produce high-purity manganese metal. During electrolysis, manganese ions are reduced at the cathode to form metallic manganese, while oxygen is evolved at the anode [28]. The electrolyte typically consists of manganese sulfate in a sulfuric acid solution.



Fig. 3 An illustration of flow for the extraction of high-purity manganese

2.3 Sintering of Manganese

Sintering is a thermal process used to compact and form solid materials from powders [44]. This process involves heating the powdered material below its melting point until its particles adhere to each other. The primary driving force for sintering is the reduction of surface energy, achieved through atomic diffusion mechanisms such as surface diffusion, grain boundary diffusion, and volume diffusion. Particle surfaces begin to bond, forming necks between them. Surface diffusion primarily dominates at this stage, leading to minor densification. Neck growth continues, and pore channels between particles shrink. Grain boundary and volume diffusion become significant, leading to densification and grain growth [45]. The remaining pores become isolated and shrink further, eventually disappearing if the process is fully optimized. Grain growth continues, and the material achieves near-full density. Several factors influence the efficiency and outcome of the sintering process, smaller particles with a narrow size distribution tend to sinter more effectively due to their larger surface area and higher driving force for diffusion [46]. Higher sintering temperatures and longer durations enhance atomic diffusion, promoting densification and grain growth. However, excessive temperature can cause grain coarsening. The sintering environment, including the presence of inert gases or vacuum, affects the oxidation and reduction reactions of the material [47]. Applying external pressure during sintering (as in hot pressing or spark plasma sintering) can significantly enhance densification and reduce sintering time.

Conventional sintering involves heating manganese powders in a furnace under a controlled atmosphere [48]. Manganese powder is compacted into a desired shape and then heated in a furnace. The temperature is typically set between 1100°C and 1400°C, below the melting point of manganese. The process occurs in an inert atmosphere or vacuum to prevent oxidation. Simple and cost-effective, suitable for large-scale production. Longer processing times and the potential for non-uniform heating, lead to inhomogeneous microstructures. SPS, also known as field-assisted sintering, applies an electric current directly to the powder compact, generating heat internally [49]. A pulsed electric current passes through the powder compact, causing rapid heating. The sintering occurs under simultaneous application of pressure and heat, typically within a few minutes at temperatures lower than conventional sintering. Rapid sintering, enhanced densification, fine-grained microstructures, and lower sintering temperatures. High equipment cost and limited scalability for large components. Microwave sintering utilizes microwave energy to heat the material, providing volumetric heating rather than surface heating [50]. Manganese powder compacts are exposed to microwave radiation, which induces heating throughout the material. This results in uniform and rapid heating, thus ensuring efficient sintering. Shorter processing times, increased energy efficiency, and uniform distribution of temperature are seen. Complex control systems and potential issues regarding materials' transparency to microwaves are realized [51]. Microstructural investigation involves the study of the inner structure of the sintered manganese products for assessing grain size, porosity, and phase distribution [52]. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) provide high-resolution images of the microstructure. Optical microscopy is a valuable means to observe at a large scale [53]. Complete understanding of microstructural properties aids in relating processing conditions to mechanical properties and the performance of sintered materials. Mechanical properties of sintered manganese products, including hardness, tensile strength, and fracture toughness, are essential for their application in industrial environments [54]. Tensile testing, fracture toughness testing, and hardness testing (e.g., Rockwell or Vickers) are conventional tests for determining mechanical properties. The process of sintering is crucial for controlling density, grain size and any defects such as the presence of pores and cracks [55]. By analysing the chemical makeup and phase changes, it is confirmed that the sintered manganese items fulfil all regulations and requirements. X-ray diffraction (XRD) is employed to determine the crystalline phases involved, and energy-dispersive X-ray spectroscopy (EDS) and inductively coupled plasma mass spectrometry (ICP-MS) are employed to determine the elemental composition [56]. A precise understanding of chemical composition and phases is required for the prediction of the material's performance under a wide range of applications, including wear resistance, corrosion resistance, and electrical conductivity. Manganese sintering is a sophisticated process for compacting manganese powders into dense and hard structures [57].

A detailed understanding of the major mechanisms of sintering, i.e., atomic diffusion and densification phases, is important for process optimization. The different sintering methods, viz., conventional sintering, spark plasma sintering, and microwave sintering, possess different advantages and disadvantages. Each process influences the microstructural characteristics, mechanical properties, and ultimate quality of the resulting sintered materials. By microstructure analysis, mechanical property testing, and chemical composition analysis, thorough characterization guarantees manganese materials of high quality for broad industrial applications [58]. As the demand for advanced materials continues to grow, innovations in sintering technologies will play a vital role in meeting the stringent requirements of modern industries.

Table 2 Comparison of manganese sintering techniques

Sintering Technique	Process Description	Advantages	Challenges	References
Conventional Sintering	<ul style="list-style-type: none"> • Heating manganese powders in a controlled atmosphere furnace. • Temperature range: 1100°C-1400°C. Conducted in an inert atmosphere or vacuum. 	<ul style="list-style-type: none"> • Simple and cost-effective. • Suitable for large-scale production. • Well-established process. • High flexibility in batch sizes. 	<ul style="list-style-type: none"> • Longer processing times. • Non-uniform heating Potential for inhomogeneous microstructures Higher energy consumption due to extended heating periods. 	[48,49]
Spark Plasma Sintering (SPS)	<ul style="list-style-type: none"> • Direct application of pulsed electric current through powder compact. • Simultaneous application of pressure and heat. • Rapid heating within minutes. • Lower temperatures than conventional sintering. 	<ul style="list-style-type: none"> • Rapid sintering process. • Enhanced densification. • Fine-grained microstructures. • Lower sintering temperatures. • Better control over grain growth. • Improved mechanical properties. 	<ul style="list-style-type: none"> • High equipment cost. • Limited scalability for large components. • Complex process control requirements. • Higher operational costs. • Limited to electrically conductive materials. 	[49,50]
Microwave Sintering	<ul style="list-style-type: none"> • Utilizes microwave radiation for volumetric heating. • Direct energy coupling with material. • Uniform heat distribution throughout the sample. 	<ul style="list-style-type: none"> • Faster processing times. • Energy efficiency. • Uniform temperature distribution. • Reduced thermal gradients. • Better microstructural control. • Lower operating costs. 	<ul style="list-style-type: none"> • Complex control systems required. • Potential issues with material transparency to microwaves. • Limited penetration depth. • Challenges in temperature measurement. • Possible thermal runaway. 	[50,51]
Hot Pressing	<ul style="list-style-type: none"> • Application of mechanical pressure during heating Conducted in protective atmosphere. • Combines pressure and temperature effects. 	<ul style="list-style-type: none"> • High densification rates. • Good control over final density. • Improved mechanical properties. • Reduced porosity. 	<ul style="list-style-type: none"> • Limited to simple geometries. • High tooling costs. • Lower production rates. • Size limitations Expensive equipment. 	[52,53]

2.4 Technological and Environmental Considerations

Efficient extraction and processing of manganese are critical for optimizing resource use and reducing operational costs [59]. Several technological challenges exist in enhancing the efficiency of manganese recovery, one of the primary challenges is the high energy requirement for processes such as electrorefining, electrowinning, and thermal reduction. Innovations focus on developing energy-efficient techniques, such as advanced electrolytic cells with lower energy consumption and more effective thermal insulation materials for furnaces [60]. The products and ores of manganese need to be properly controlled to enhance the overall operating efficiency. Reduction in the requirement of human intervention and improvement in throughput has been made possible through the application of conveyor systems and robots in material handling. Moreover, sophisticated process control systems that rely on AI and ML algorithms optimize operational parameters in real-time, thereby

achieving maximum recovery rates while minimizing energy requirements [61]. The progression of technology in extraction and recovery is crucial to satisfy the growing requirements for high-purity manganese. Recovery methods in hydrometallurgy become more effective when leaching agents and catalysts improve. Due to these changes, the process needs fewer chemicals and precisely targets the presence of manganese in the samples. Likewise, using bioleaching with microorganisms for extracting manganese has made a meaningful difference in the industry.

Studies on genetically modified bacteria and fungi capable of existing under extreme environments have created new avenues for the treatment of low-grade ores [62]. Developing materials for electrodes that are both conductive and durable makes electrolytic processes work more efficiently. Optimization of design at cell levels assists in the utilization of less energy and having products of higher quality recovered [63]. Recycling and treatment of waste are very crucial to assist in reducing the environmental impacts brought about by manganese processing and extraction; moreover, sludge production from precipitation and leaching activities is a principal environmental issue [64].

Development of new sludge treatment technologies such as membrane filtration and advanced oxidation processes facilitates the recovery of valuable metals from sludge while minimizing its volume and toxicity. Tailings, which represent the waste material after ore processing, are of greatest concern to manage. Methods like dry stacking and paste backfill, in which tailings are blended with cement to backfill excavated pits, minimize the risk of environmental pollution and enhance land restoration [65]. Recycling of manganese from industrial waste spent batteries and other secondary materials lessens the demand to mine primary ores. Research into mechanical, hydrometallurgical, and pyrometallurgical recycling technologies facilitates the recovery of manganese with high efficiency, thereby fostering a circular economy. Minimizing the environmental footprint of manganese mining and processing is the need of the hour for sustainable development. Technological improvement in emission control devices, i.e., scrubbers, electrostatic precipitators, and catalytic converters, minimizes the release of toxic gases and particulate matter in manganese processing. These guidelines help make certain that air quality is kept within the necessary standards. With closed-loop systems and treatments, water use is decreased and natural water is kept clean [23]. Applying reverse osmosis and better filters to water cleans it and enables us to use it repeatedly. When solar and wind energy are used in manganese processing, less fossil fuel is needed and this also reduces greenhouse gas emissions. Mixing renewable energy with energy storage increases the sustainability of manganese production [67]. Strong regulations help ensure the environmental issues from manganese mining and processing are reduced to the lowest level possible. Following environmental laws such as the Clean Air Act, Clean Water Act and hazardous waste management regulations prevents manganese producers from making their environmental problems worse. Regularly checking and recording emissions, effluents and wastes are important to confirm compliance with regulations [68]. Following specific standards such as ISO 14001 and ISO 50001, is a way to demonstrate both environmental care and a desire to improve. Implementing CSR actions that focus on caring for the environment, participating in local communities and sustainable resource use is helpful for a positive public image of manganese producers. Organization may participate in CSR by planting trees, teaching locals about sustainable living or providing local community infrastructure [69]. Technology and the environment are both important in making mining and processing of manganese more sustainable [70]. Using better technologies such as energy-saving approaches and AI, helps manage important issues in technology.

The use of hydrometallurgical processes, bio-leaching and electrolysis greatly boosts the efficiency and eco-friendly manganese production. Waste handling and recycling should be conducted in an environmentally sound manner in order to mitigate environmental effects. Developments in sludge treatment, tailing control, and recycling are important parameters driving a circular economy, thereby decreasing the demand for primary ore extraction and limiting environmental hazards [71]. Introducing emission control practices, building suitable water management systems and depending on renewable energy sources are big steps towards making manganese processing environmentally safe and crucial for sustainable growth. Both local and international rules should be followed by manganese producers to avoid risks to nature and ensure protection.

The use of corporate social responsibility helps a company become more ecologically responsible and engaged with the community [72]. With the growing demand for manganese, continued research and advancements in technological innovation and environmental management will be critical. This will guarantee that the extraction and processing of manganese are up to industrial standards as well as promote an environmentally friendly and sustainable future.

3. Future Perspectives and Research Directions

Future progress in manganese mining and recovery will come from new technologies, eco-friendly methods and identifying the key priorities for future research. Following these paths will make it possible to fulfil the rising demand for manganese in a way that is kind to both the environment and the economy.

Emerging technologies are the key to revolutionizing the manganese industry by making it more efficient, cost-effective, and environmentally friendly [73]. The application of nanotechnology for manganese extraction and recovery is very promising. Nanomaterials can be used to enhance the efficiency and selectivity of leaching reagents and adsorbents. Nanomaterials can assist in creating better catalysts for bioleaching which allows manganese to be extracted from poor ores and lessens the effects on nature of older extraction methods. Advances in electrochemistry such as inventing improved electrodes and electrolytes, make electrowinning and electrorefining more effective [74]. The outcome can be reduced energy consumption and manganese of higher purity.

Bioleaching using genetically engineered microorganisms is a novel area in manganese recovery. Genetically engineered microorganisms can be designed to be active even in unfavourable conditions and selectively leach manganese from refractory ores without using aggressive chemical reagents and resulting in environmental pollution [75]. The application of green methods in manganese extraction and recovery processes is essential for the long-term sustenance of the business [76]. Sustainable operations not only limit the environmental impact but also ensure economic viability in the long term.

Precedence must be given to manganese recycling from alternative sources, i.e., spent batteries and industrial wastes. Recycling technology development can improve the efficiency of manganese recycling, decrease the dependency on primary ore mining, and promote the development of a circular economy [77]. For instance, the advancement in hydrometallurgical and pyrometallurgical technologies allows manganese to be more efficiently recovered and with less environmental impact from complicated waste streams. Solar and wind renewable energy integration into manganese extraction and processing operations can help cut down carbon emissions considerably. Besides, hybrid systems involving the utilization of renewable energy coupled with energy storage systems provide an energy guarantee, hence making manganese production sustainable. The principles of green chemistry can be adopted and applied to the manganese extraction processes to limit the use of toxic chemicals and lower the production of toxic waste. Development of solvent extraction techniques utilizing green solvents, along with the utilization of biodegradable leaching reagents, provides promising avenues to the sustainable extraction of manganese [78]. To fully exploit the potential of the emerging technologies and the green practices, several important areas must be examined more closely, research and development into new materials for electrochemical applications, such as new electrode coatings and solid electrolytes, can lead to improved efficiency and longer life for electrowinning and electrorefining operations. Understanding at the molecular level of the interaction of the materials and the manganese ions will be critical.

Further study into the genetic alteration of microbes for bioleaching is likely to uncover new directions in the recovery of manganese from low-grade and complex ores [79]. Fully understanding what drives metabolism and finding the optimal conditions for microbes is a major research objective. Large-scale studies (LCAs) of the rehabilitation of manganese can provide insightful information about its environmental impact. Undertaking an LCA can guide more sustainable decision making by highlighting the areas where improvements can be made and reducing the wasting of resources. The efficiency of manganese recovery and extraction can be improved with the help of emerging advancements in artificial intelligence and machine learning techniques. Better control over operating parameters can be achieved by applying predictive models and online monitoring systems, leading to higher recovery and lower negative impacts on the environment [80]. Recycling and future production of manganese depend on the incorporation of emerging technologies, green approaches, and targeted research. Nanotechnology, electrochemistry, and biotechnology advances have promising potential of enhancing the environmental sustainability and efficiency of manganese production [81]. The embracement of circular economy principles, green chemistry principles, and renewable energies will also guarantee a sustainable manganese industry.

Achieving these targets involves continuous research in materials science, microbial genomics, lifecycle assessment and process optimization. Paying attention to these areas allows the manganese industry to supply future needs while limiting its effects on the environment and ensuring long-term security.

4. Conclusion

This review has pointed out various important areas of manganese extraction, recovery and sintering and the special status of the nature of manganese-containing ores in those processes. For example, the industry can improve its efficiency and harm the environment less by using advanced electrochemical methods, nanotechnology and biotechnological approaches. Initiatives like switching to renewable sources and making recycling easier are part of the world's attempts to lessen damage to the environment and introduce a circular economy. To achieve these innovations, careful research must be done in materials science, microbial genomics and process improvement. Proper evaluations of the lifecycle will guide creating new processes, leading to meeting economic and environmental goals. The coming advances in manganese extraction are most likely at the intersection of improving technology and caring for the environment. Being aware of the increased demand, the industry needs to incorporate new technologies and greener methods to cope with it and waste less resources.

Since modern economies focus on sustainability, the manganese industry is prepared to greatly help achieve sustainable growth.

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Conflict of Interest

Authors declare that there is no conflict of interests regarding the publication of the paper.

Author Contribution

GYE conceived and wrote the manuscript, while AOO, BJO, AFO, and NW proofread and made edits to it.

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