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Review

Mineral-Based Magnesium Extraction Technologies: Current and Future Practices

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Abstract

Magnesium is a valuable industrial metal prized for its strength and reactivity. Traditionally, magnesium was extracted from seawater and brines. However, to meet the rising global demand, it is now primarily sourced from mineral deposits. This shift has sparked renewed interest in extracting magnesium from non-saline sources, including carbonates, silicates, halides, oxides, and hydroxides. This review examines the extraction technologies currently used for these mineral-based resources, including pyrometallurgical, hydrometallurgical, and electrometallurgical methods. Each method is assessed based on the reactions involved in the transformation, operational principles, efficiency, and energy requirements. The review emphasizes the importance of mineral pretreatment—thermal, mechanical, and chemical—in improving magnesium recovery, especially from refractory silicates. By summarizing recent advancements and process innovations, the review aims to inform future research and industrial practices, and support the development of sustainable, cost-effective, and scalable magnesium extraction strategies.

Keywords: magnesium; Mg-bearing minerals; hydrometallurgy; pyrometallurgy; electrometallurgy; pretreatment

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1. Introduction

Magnesium is the eighth most abundant element in the Earth's crust and is widely distributed in both aqueous and solid forms. In seawater and natural brines [1–16], including desalination reject streams and salt lakes [17–28], magnesium predominantly exists as Mg^{2+} ions associated with chloride and sulfate salts. Other aqueous sources include hydrometallurgical leachates derived from magnesium-bearing ores [29–41]. Solid-phase magnesium occurs in various minerals, classified into four categories: oxides and hydroxides, carbonates, silicates, and halide evaporites. These minerals differ in magnesium content, extractability, and geological origin, as summarized in Table 1. In addition to primary resources, secondary sources such as fly ash [42,43], flue gas [44], phosphate rock [29,45], and ferrochrome slag [46] are also considered viable feedstocks for magnesium recovery.

The chemical and physical properties of magnesium make it attractive for structural and functional applications [47,48]. It is low in density yet high in strength-to-weight ratio. It is also easily cast and machined, supporting its widespread use in engineering alloys and composites that enhance mechanical performance and energy efficiency [47,49–51]. Its versatility underlies its adoption across a range of industries, particularly in mass-sensitive sectors such as automotive, aerospace, and electronics [52–60]. Recent studies have also

highlighted magnesium's critical role in developing high-performance composites, where microstructural engineering significantly enhances mechanical properties and machining performance [61,62]. Magnesium's electronic configuration ($1s^2$ $2s^2$ $2p^6$ $3s^2$) and low ionization energies favor the formation of the divalent Mg^{2+} ion, with a standard reduction potential of $E^\circ = -2.375$ V for the Mg^{2+}/Mg couple. This high reactivity is the basis for its use in electrochemical systems, as a sacrificial anode for corrosion protection [63–67], and as a refractory material [68–72]. In addition, magnesium's biocompatibility enables its use in biomedical implants [73–76], and its electrochemical properties are increasingly being exploited in batteries and environmental technologies [77–82]. More recently, magnesium-rich silicate minerals, such as olivine and serpentine, have received attention for their potential in carbon dioxide capture and sequestration through mineral carbonation. In this process, magnesium reacts with CO_2 to form stable magnesium carbonates, enabling the long-term solid-phase storage of the greenhouse gas [83–99]. This emerging application further underscores magnesium's growing relevance in sustainable and circular material technologies.

Table 1. Main magnesium-bearing raw minerals.

Mineral Category	Mineral's Name	Chemical Formula	Mg Content (wt%)	Availability
Oxide and hydroxide	Periclase	MgO	60.30	Occurs as a synthetic product; natural deposits are limited and localized (Mainly in Russia, the U.S., and China).
	Brucite	$Mg(OH)_2$	41.70	
Carbonate	Magnesite	$MgCO_3$	28.83	Extremely abundant worldwide, >50 billion tonnes with major deposits in China, Russia, and Turkey.
	Dolomite	$CaMg(CO_3)_2$	13.18	
Silicate	Forsterite	Mg_2SiO_4	34.55	Vast global abundance, >100 billion tonnes. Common in ultramafic rocks especially in ophiolite belts and metamorphic deposits, with major reserves in China, India, Iran, and the U.S.
	Serpentine	$Mg_3Si_2O_5(OH)_4$	26.31	
	Olivine	$(Mg,Fe)_2SiO_4$	25.37	
	Enstatite	$MgSiO_3$	24.21	
	Talc	$Mg_3Si_4O_{10}(OH)_2$	19.23	
	Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$	14.96	
Evaporite halides	Bishofite	$MgCl_2 \cdot 6H_2O$	11.96	Extensive in brine deposits; major reserves in Canada, Russia, and the U.S.
	Carnallite	$KMgCl_3 \cdot 6H_2O$	8.75	

From a production standpoint, large-scale electrolytic production of metallic magnesium began historically with the processing of molten carnallite in Germany in 1886 [100], following Davy's first laboratory synthesis of magnesium sulfate via electrolysis in 1808 [47]. Although industrial magnesium production relies on energy-intensive extraction processes from various raw materials, two primary methods are employed: electrolysis of magnesium chloride and thermal reduction of magnesium oxide [101–108]. Electrolytic production, which is typically performed using molten magnesium chloride, remains the dominant industrial method due to its lower energy costs and greater efficiency [82,109,110]. In contrast, the Pidgeon process and other thermal reduction methods are more energy-intensive and generally less cost-effective [82,111].

This review provides a comprehensive examination of magnesium, including its geological occurrence, extraction technologies, and potential applications. First, we explore the mineralogical sources of magnesium, such as oxides, hydroxides, carbonates, silicates, and evaporite-hosted deposits. Next, we critically assess the three primary extraction pathways—pyrometallurgical, hydrometallurgical, and electrometallurgical—with a focus on nuances in leaching strategies tailored to specific mineral types. We pay special attention to the challenges and innovations in extracting magnesium from silicate-rich feedstocks. Integrating insights from mineralogy, reaction chemistry, and process engineering, this review establishes a framework to guide future research and industrial strategies for magnesium valorization, particularly in sustainable material systems and emerging environmental applications.

2. Magnesium-Bearing Mineral Sources

Magnesium occurs in a wide range of mineralogical forms, each with distinct geochemical behaviors, structural characteristics, and levels of industrial relevance. Broadly classified as oxides and hydroxides, carbonates, silicates, and halides (Table 1), these minerals differ in abundance, formation environments, physicochemical properties, and extractive potentials. Although carbonates, such as magnesite, have traditionally dominated primary magnesium production, there is a growing interest in silicate minerals, such as olivine and serpentine, due to their potential for sustainable applications, including CO_2 mineralization and circular economy initiatives. Comprehensive understanding of the mineralogical diversity and geological context of these phases is essential for advancing both established and emerging magnesium sourcing technologies.

2.1. Oxide and Hydroxide Minerals

Periclase (MgO) is the natural analog of synthetic magnesia and typically forms in water-deprived and/or high-temperature environments. In most geological settings, it is unstable and readily undergoes retrograde alteration to brucite, $Mg(OH)_2$ [112].

Brucite ($Mg(OH)_2$) is a crystalline form of magnesium hydroxide, characterized by its waxy to glassy appearance and colors ranging from white to pale-green or gray. Brucite, with its relatively soft texture and low density, provides a higher magnesium content than other ores and is used as both an environmentally friendly flame retardant and a viable source of metallic magnesium. It is commonly found in ultramafic rocks and economic deposits are typically associated with high-temperature, low-pressure metamorphic environments [91–93,112–115].

2.2. Carbonate Group Minerals

Magnesite ($MgCO_3$), containing 28.8% magnesium by weight, is primarily composed of magnesium carbonate with minor impurities of calcium, iron, and manganese, and generally appears as a white mineral with a crystalline structure similar to calcite. It typically forms through metamorphic processes when magnesium-rich rocks interact with carbonate-rich solutions [82].

Dolomite ($MgCO_3 \cdot CaCO_3$), a double carbonate of magnesium and calcium, is colorless and exhibits a diamond-shaped crystal structure. It typically forms through the alteration of calcite in the presence of magnesium ions. It contains minimal impurities such as iron and manganese, making it a valuable source of magnesium for industrial applications [82].

2.3. Silicate Group Minerals

Magnesium-bearing silicate minerals, including olivine, forsterite, enstatite, serpentine, tremolite, and talc, are a diverse group of compounds known for their high magnesium content and complex structures. These minerals, typically found in mafic, ultramafic, and metamorphic rocks, are crucial for industrial applications such as magnesium extraction, metallurgy, refractories, foundry, and environmental technologies, such as CO_2 sequestration and mineral carbonation.

Olivine consists of magnesium–iron silicates, of which, forsterite (Mg_2SiO_4) and fayalite (Fe_2SiO_4) are key constituents of the Earth's mantle. They are characterized by their green color and high magnesium content. They are important for geological studies and industrial applications. Forsterite, the magnesium-rich endmember, is particularly valued for its orthorhombic crystal structure, high thermal stability, and suitability for processes such as mineral carbonation.

Enstatite ($MgSiO_3$) is a magnesium-rich silicate mineral within the pyroxene group, commonly occurring in igneous and metamorphic rocks, especially in ultramafic and high-temperature settings. Featuring an orthorhombic crystal structure, enstatite is significant for understanding mantle rock compositions and serves as a potential source of magnesium.

Serpentine ($Mg_3Si_2O_5(OH)_4$) is a group of hydrated magnesium silicate minerals, including the antigorite, lizardite, and chrysotile polymorphs, known for their green color and formation through the alteration of olivine and other magnesium-rich silicates. Featuring a layered structure of tetrahedral silicates interspersed with $Mg(OH)_2$ layers, serpentine contains 26.3% magnesium by weight. Serpentine, widely found in metamorphic environments, has become a valuable resource for industrial magnesium production and is often obtained as a by-product of asbestos extraction.

Tremolite ($Ca_2Mg_5Si_8O_{22}(OH)_2$) is a calcium–magnesium silicate mineral in the amphibole group, typically found in areas undergoing low- to medium-grade metamorphism. Commonly associated with serpentine, tremolite is recognized for its fibrous structure, which poses both industrial utility and health risks due to its asbestos-like characteristics.

Talc ($Mg_3Si_4O_{10}(OH)_2$) is a soft, layered magnesium silicate mineral prized for its softness and hydrophobic nature. Commonly used in ceramics, cosmetics, and as a lubricant, talc forms through the metamorphic transformation of magnesium-rich rocks like dolomite or serpentine and is noted for its smooth, greasy texture, and its white to green color.

2.4. Evaporate Halides

Magnesium can also be sourced from highly soluble evaporite minerals, primarily recovered from saline lakes and marine brines via solar evaporation or solution mining.

Bischofite ($MgCl_2 \cdot 6H_2O$) is a transparent, hygroscopic halide mineral containing 11.96 wt% magnesium. It forms during the late stages of brine evaporation and is primarily extracted through solar evaporation. Known for its distinctive chip-like structure, bischofite is used in de-icing applications and various chemical processing industries.

Carnallite ($MgCl_2 \cdot KCl \cdot 6H_2O$) is an evaporite halide mineral made up of hydrated potassium and magnesium chloride, containing 8.75% magnesium by weight. It varies in color from yellow to white and serves as a dual resource, providing both potassium for fertilizers and magnesium ore.

3. Magnesium Extraction Processes

Magnesium extraction from minerals, which includes pyrometallurgical methods like thermal reduction of magnesium oxide, hydrometallurgical techniques, and electrometallurgical processes such as electrolysis of magnesium chloride, is crucial for reducing production costs and minimizing environmental impact.

Magnesium can be extracted through a variety of methods, including commercially established technologies such as the Pidgeon process, electrolytic reduction, and precipitation, as well as emerging approaches like advanced hydrometallurgical processes.

Pyrometallurgical processes generally have the highest carbon footprint due to their reliance on coal-based reductants and high temperatures. Hydrometallurgical methods lower direct emissions by reducing energy use but shift the environmental burden toward chemical consumption, effluent treatment, and solid waste management. Electrometallurgical approaches, particularly molten salt electrolysis, offer a lower long-term footprint when powered by renewable electricity. Moreover, silicate feedstocks present additional opportunities for carbon capture through mineral carbonation, enhancing the overall sustainability of magnesium production. Although detailed life–cycle assessments (LCAs) remain limited, current evidence suggests that combining renewable energy with electrometallurgy and integrating CO_2 sequestration strategies provides the most sustainable pathways.

Cost plays a decisive role in selecting magnesium extraction routes. Pyrometallurgical processes like the Pidgeon method are simple and low in capital demand but highly energy-intensive, with energy accounting for over half of production costs, making them viable mainly where cheap energy is available. Hydrometallurgical methods reduce energy use but incur higher expenses for reagents, effluent management, and pretreatment of low-grade ores, though they can be cost-effective for secondary feedstocks such as slags. Electrometallurgical processes, particularly molten salt electrolysis, require high upfront investment but offer lower operating costs and scalability when supported by inexpensive or renewable electricity. Overall, pyrometallurgy is less sustainable but still dominant in energy-abundant regions, hydrometallurgy balances energy and chemical costs, and electrometallurgy provides the most favorable long-term economics under access to green power.

3.1. Pyrometallurgy

Thermal methods of extracting magnesium involve heating magnesium-bearing minerals with various reducing agents at high temperatures in a process called thermal reduction. The primary ore minerals used in these processes are dolomite and, to a lesser extent, magnesite. During calcination in a kiln, the raw materials produce a mixture of magnesium oxide and calcium oxide, as shown by Equations (1) and (2).

$$MgCO_3 \cdot CaCO_{3(s)} \rightarrow MgO \cdot CaO_{(s)} + 2CO_{2(g)} \quad (1)$$

$$MgCO_{3(s)} \rightarrow MgO_{(s)} + CO_{2(g)} \quad (2)$$

Thermal reduction methods, such as silicothermic, aluminothermic, and carbothermic processes, operate at high temperatures ranging from 900 °C to 1900 °C, with the efficiency of magnesium extraction from magnesite or dolomite being significantly influenced by both the temperature and the chosen method [116–119].

Silicothermia process is the predominant commercial method for production of metallic magnesium from calcined dolomite. In this method, magnesium oxide and lime are mixed with ferrosilicon and heated, producing metallic magnesium and a dicalcium silicate slag, as depicted in Equation (3) [82]:

$$2CaO + 2MgO + Si(Fe) \rightarrow 2Mg + Fe + Ca_2SiO_4 \quad (3)$$

Likewise, the reduction reactions of magnesia (MgO) and lime (CaO) by silicon (Si) at elevated temperatures can be represented by Equations (4) and (5), respectively.

$$2MgO_{(s)} + Si_{(s)} \rightarrow 2Mg_{(g)} + SiO_{2(s)} \quad (4)$$

$$2CaO_{(s)} + Si_{(s)} \rightarrow 2Ca_{(s)} + SiO_{2(s)} \quad (5)$$

Magnesium is produced as vapor during the thermal reduction process and is condensed into a solid state through cooling. Alumina may be added to lower the slag's melting point. The condensed magnesium undergoes remelting, refinement, and casting into ingots, billets, and slabs after impurities are removed and alloying elements are added. Despite being energy-intensive, this process is widely used for its efficiency in producing high-purity magnesium.

The **aluminothermia** process employs aluminum which acts as the reducing agent to produce magnesium by reducing calcined dolomite, sometimes with added magnesite, as shown in Equation (6) [82].

$$3MgO_{(s)} + 2CaO_{(s)} + 2Al_{(l)} \rightarrow 3Mg_{(s)} + 2CaO \cdot Al_2O_{3(s)} \quad (6)$$

The aluminothermic process operates at lower temperatures than other thermal methods, making it more energy-efficient, but the high cost of aluminum remains a major drawback. Innovations like the Heggie process [120], which uses aluminum scrap in an argon atmosphere, seek to optimize this approach. The initial reduction temperature of magnesium oxide in calcined dolomite with aluminum is around 720 °C, and using aluminum powder can lower the reaction temperature and enhance reaction speed, resulting in higher magnesium yields [121]. Studies have shown that aluminum powder as a reducing agent outperforms ferrosilicon in magnesium extraction under vacuum conditions [122].

The **carbothermia** process involves the reduction of magnesium oxide with carbon (coke). The reaction is represented as Equation (7) [82].

$$MgO_{(s)} + C_{(s)} \leftrightarrow Mg_{(g)} + CO_{(g)} \quad (7)$$

The carbothermic method is less commonly used for magnesium extraction due to its high activation energy and the risk of reverse reactions during slow cooling, which complicates production. Rapid cooling is required to prevent these reverse reactions, but it results in very fine magnesium powder, making further processing challenging. An alternative approach using calcium carbide (CaC_2), as the reducing agent can be performed at slightly lower temperatures (1120 °C to 1140 °C), but the high cost of calcium carbide remains a significant drawback.

Figure 1 depicts a general flow chart that summarizes the major steps of the pyrometallurgical processes for magnesium production.

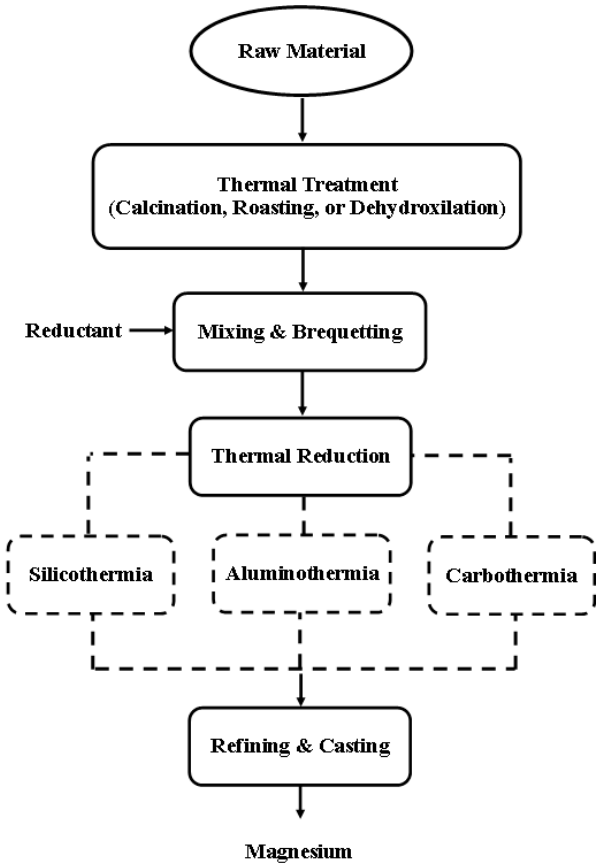

Figure 1. Flowchart of pyrometallurgical route for magnesium production.

In summary, thermal reduction processes for extracting magnesium from minerals like dolomite and magnesite are highly temperature-dependent and require careful selection of reducing agents. While effective, these methods are energy-intensive, prompting ongoing

research to enhance efficiency and lower costs [118,123,124]. Optimal temperatures vary by method; for instance, the Pidgeon process operates between 1200 °C and 1400 °C [125], while the aluminothermic process requires 1473 K to 1573 K [119]. Precise temperature control is crucial for maximizing efficiency and minimizing energy consumption. The operating conditions for various thermal methods used in magnesium extraction from mineral resources are outlined in Table 2.

Table 2. Different processes of thermal reduction methods and their operating conditions [82].

Thermal Reduction	Main Process	Additive	Pressure	Temperature (°C)
Silicothermia	-Pidgeon	-Ferrosilicon	10 mm-Hg	1200–1400
	-Magnetherm	-Ferrosilicon, Al_2O_3, Al	1 atm	1300–1700
	-Bolzano	-Ferrosilicon, Al_2O_3	3 mm Hg	1200
Aluminothermia	Heggie	Al scrap	1 atm Ar	1500 (arc plasma)
Carbothermia		Coke	1 atm	1900
		CaC_2	1 atm	1120–1140

3.2. Hydrometallurgy

Thermal reduction remains the primary method for extracting magnesium from minerals such as dolomite and magnesite. However, growing interest in solution-based methods has prompted the development of hydrometallurgical alternatives. Leaching is a key technique for recovering magnesium from sources such as carbonates, silicates, oxides, hydroxides, and hydrated salts. Organic and inorganic acids, as well as alkaline salt solutions, are commonly used, and the choice of reagent depends on the specific mineral. The efficiency of magnesium recovery depends significantly on operational parameters such as temperature and reagent concentration.

Various separation and purification techniques can be employed to extract magnesium from aqueous solutions, including seawater, brines, and leachates produced by hydrometallurgical processes. These techniques include crystallization, chemical precipitation, solvent extraction, ion exchange, membrane separation, electrolysis, electrodialysis, and adsorption [1–3,21–25,126–133]. Crystallization and precipitation are often the initial steps in isolating magnesium salts from solutions. The recovery method selected depends on the concentration and composition of the feed solution, which varies depending on the origin of the magnesium-rich stream [1,4–6,21,134–136]. For concentrated sources, such as inland brines, solar evaporation in large ponds is commonly employed, particularly in arid climates. In contrast, chemical precipitation is generally favored for more dilute sources, such as seawater or acidic leachates [22,30,126,137]. Alkaline reagents, including NaOH [7,10,26,138–140], $Ca(OH)_2$ [141,142], NH_4OH [27,28,143], and Na_3PO_4 [144], are typically used to precipitate brucite.

Mg extraction from periclase or brucite: Leaching magnesium from its oxide and hydroxide minerals is generally simpler than from other Mg-bearing sources. This makes converting the resulting leachate into magnesium chloride easy, either directly or through a few simple steps. Magnesium chloride is a precursor to electrometallurgical extraction of metallic magnesium. Common leaching agents include hydrochloric acid, ammonium-based solutions, and various organic acids.

- ***HCl leaching*:** Brucite readily dissolves in hydrochloric acid, following the reaction described in Equation (8) [145,146]. Brucite can also be calcined to magnesia (Equation (9)) [8,147] whereby Mg is then leached by the way of Equation (10) [30,148]:

$$Mg(OH)_{2(s)} + 2HCl_{(aq)} \rightarrow MgCl_{2(aq)} + 2H_2O_{(l)} \quad (8)$$

$$Mg(OH)_{2(s)} \rightarrow MgO_{(s)} + H_2O_{(g)} \quad (9)$$

$$MgO_{(s)} + 2HCl_{(aq)} \rightarrow MgCl_{2(aq)} + H_2O_{(l)} \quad (10)$$

Subsequently, magnesium chloride can be purified from dissolved metal ions using alkali precipitation, where pure $Mg(OH)_2$ powder is added to precipitate the impurities as metal hydroxides, followed by the crystallization of $MgCl_2 \cdot 6H_2O$ through evaporation (Figure 2) [31].

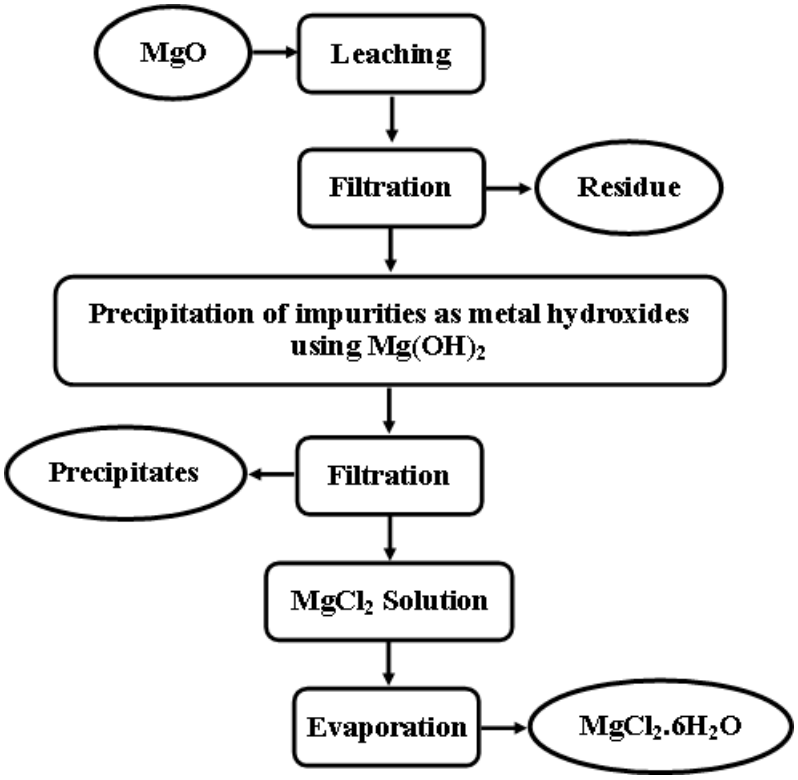

Figure 2. Flowchart of magnesium chloride recovery from MgO by HCl leaching process.

- ***Ammonium chloride leaching***: Aqueous NH_4Cl can selectively extract magnesium from $Mg(OH)_2$-containing solids, resulting in an aqueous $MgCl_2$ solution while simultaneously regenerating NH_3. The primary reaction involved in this process is as follows [149]:

$$Mg(OH)_{2(s)} + 2NH_4Cl_{(aq)} \rightarrow MgCl_{2(aq)} + 2NH_{3(g)} + 2H_2O_{(l)} \quad (11)$$

Ammonium chloride or calcium chloride, combined with carbon dioxide, has also been effectively utilized to selectively leach magnesia. The resulting magnesium chloride is treated with ammonia and carbon dioxide to precipitate magnesium carbonate, which is then calcined, briquetted, and sintered to produce high-purity magnesia. Additionally, all reagents used throughout the process are recovered and recycled efficiently [150].

- ***Organic acid leaching***: Dissolving MgO with organic acids offers benefits such as mild reaction conditions and a lower environmental impact compared to inorganic acids. Organic acids like acetic acid react with MgO, producing soluble magnesium salts and water. For instance, acetic acid can gradually dissolve magnesium from MgO, forming magnesium acetate (Equation (12)).

$$MgO_{(s)} + 2CH_3COOH_{(aq)} \rightarrow Mg^{2+}_{(aq)} + 2CH_3COO^-_{(aq)} + H_2O_{(l)} \quad (12)$$

The effectiveness of this process depends on the specific surface area of MgO, making it suitable for selective leaching and a practical option for magnesium extraction in various applications [151].

The combined action of hydroxybenzoic acid and tetrasodium dicarboxymethyl aspartate enabled efficient magnesium extraction from brucite, achieving 99.48% leaching efficiency and producing high-purity $MgCO_3$ [152].

- ***CO_2 leaching*:** Magnesia derived from calcination often contains complex oxide impurities, such as SiO_2, Al_2O_3, Fe_2O_3, and CaO, which complicate the refinement of magnesium products. To overcome this issue, a CO_2 leaching technique has been developed where MgO reacts with aqueous CO_2 to form soluble magnesium bicarbonate ($Mg(HCO_3)_2$) [153–155]. This method selectively dissolves magnesia, leaving impurities behind, and produces a solution that can be decomposed through heating or aeration to form basic magnesium carbonate. This carbonate is then further processed to yield high-purity magnesia [150].

The gas–liquid partition of CO_2 (Equation (13)) is improved under low temperatures and high CO_2 pressures, while the formation of carbonate and bicarbonate (Equation (14)) is enhanced under alkaline conditions [156,157].

$$CO_{2(g)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)} \quad (13)$$

$$H_2CO_{3(aq)} \rightleftharpoons H^+_{(aq)} + HCO^-_{3(aq)} \rightleftharpoons 2H^+_{(aq)} + CO^{2-}_{3(aq)} \quad (14)$$

The process of extracting magnesium from magnesia through pressure carbonation can be described by the following reactions [141,150]:

$$MgO_{(s)} + H_2O_{(l)} \rightleftharpoons Mg(OH)_{2(aq)} \quad (15)$$

$$Mg(OH)_{2(aq)} + 2CO_{2(aq)} \rightleftharpoons Mg(HCO_3)_{2(aq)} \quad (16)$$

In fact, $Mg(OH)_2$ reacts with carbonic acid formed from the dissolution of CO_2 in water (Equations (13) and (14)), leading to the reaction described in Equation (17) [20]:

$$Mg(OH)_{2(aq)} + H_2CO_{3(aq)} \rightleftharpoons Mg^{2+}_{(aq)} + CO^{2-}_{3(aq)} + 2H_2O_{(l)} \quad (17)$$

The overall reaction can be summarized by Equation (18):

$$MgO_{(s)} + 2CO_{2(g)} + H_2O_{(l)} \rightleftharpoons Mg^{2+}_{(aq)} + 2HCO^-_{3(aq)} \quad (18)$$

Therefore, the solubility of MgO increases with lower temperatures and higher CO_2 pressures during the aqueous leaching process [150]. Reports indicate that employing ultrasound energy enhances the dissolution of magnesia in aqueous carbon dioxide [155,158].

Impurities such as Fe_2O_3, SiO_2, Al_2O_3, and CaO may remain undissolved or precipitate at certain pH levels. This allows them to be removed from the $Mg(HCO_3)_2$ solution via simple filtration. The solution can then be converted into high-purity MgO by heating and calcining it. Leaching caustic-calcined magnesia with carbon dioxide in the presence of water converts MgO into soluble $Mg(HCO_3)_2$ and effectively separates impurities [153]. However, a major drawback of the CO_2 leaching process is the relatively low solubility of magnesium bicarbonate. This increases capital costs when processing large volumes of solution [150]. Maintaining a high mass concentration of the magnesia slurry at controlled temperatures is essential to prevent the hydrolytic decomposition of $Mg(HCO_3)_2$ into insoluble magnesium hydroxycarbonate [154].

Mg extraction from carbonates: Dolomite and magnesite are the key feedstocks in the hydrometallurgical acid-leaching extraction processes of magnesium-rich carbonates.

- ***HCl leaching*:** Dolomite and magnesite, both magnesium-rich carbonate minerals, are widely used as feedstocks for magnesium extraction via hydrometallurgical processes [22]. One common method is the hydro-magnesium process, which involves direct acid leaching with hydrochloric acid (Figure 3) [32,33,159,160]. In this process, magnesite or dolomite reacts with HCl to form magnesium chloride, carbon dioxide, and water, as shown in Equations (19) and (20).

$$MgCO_{3(s)} + 2HCl_{(aq)} \rightarrow MgCl_{2(aq)} + CO_{2(g)} + H_2O \quad (19)$$

$$(Mg, Ca)CO_{3(s)} + 2HCl_{(aq)} \rightarrow (Mg, Ca)Cl_{2(aq)} + CO_{2(g)} + H_2O \quad (20)$$

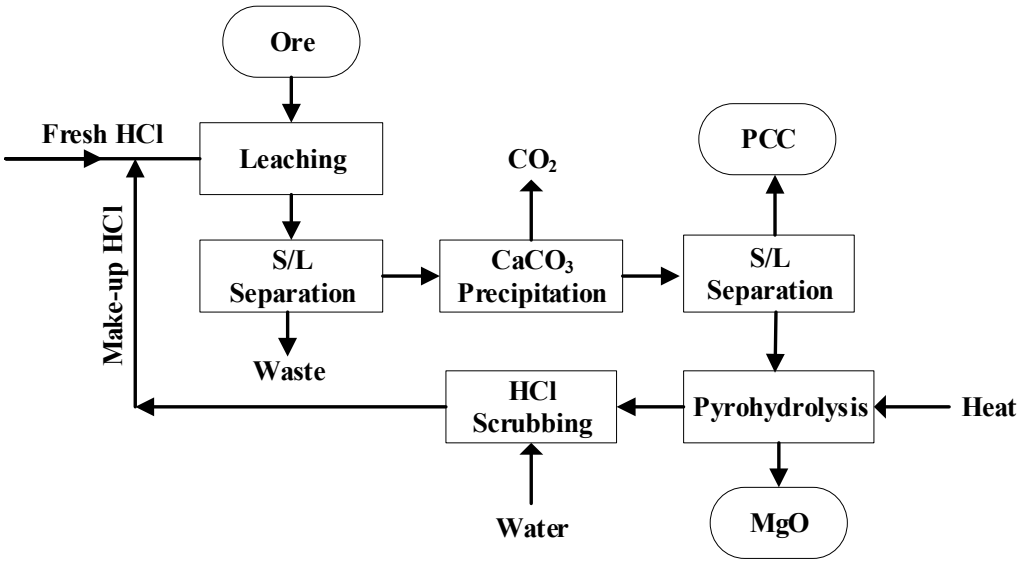

Figure 3. Leaching of Mg-rich carbonate minerals using HCl.

However, because these carbonate minerals contain metallic impurities, sulfates, and boron, the magnesium chloride solution must undergo an additional purification step to remove these contaminants before electrolysis [82].

Direct leaching of Mg-bearing carbonate minerals often results in high acid consumption and the release of carbon dioxide, which can disrupt the process. To address this, dolomite or magnesite is typically calcined to produce magnesium oxide, which is then leached with hydrochloric acid to form magnesium chloride (Equation (10)).

The Dow process exemplifies this approach: dolomite is first calcined to produce mixed oxides (Equation (1)), which are then introduced into seawater containing magnesium ions. The resulting magnesium hydroxide is reacted with hydrochloric acid (Equation (8)), which is recycled from chlorine generated during electrolysis. This closed-loop use of chlorine enhances the overall efficiency of the Dow process [82]. Calcined carbonate minerals exhibit higher reactivity, and under appropriate conditions, their dissolution rate in hydrochloric acid can effectively regulate the output of the leaching reactor [160].

- ***Salt roasting–water leaching*** The $(NH_4)_2SO_4$ roasting–water leaching process efficiently enhances magnesium recovery from magnesite, achieving a maximum extraction rate of 98.7% at 475 °C. The process follows a mixed chemical–diffusion control mechanism and allows cyclic use of reagents, offering a promising alternative for magnesite processing [161].

- ***Organic acid leaching*:** Several studies have examined the leaching of magnesium-rich carbonates using various organic acids, including citric acid [162], acetic acid [151,163–166], lactic acid [167], formic acid [168], succinic acid [169], and gluconic acid [170,171]. Organic acids offer high selectivity but limited dissolution power, making them most effective for carbonaceous compounds. They operate under mildly acidic conditions (pH 3–5), which reduces CO_2 pressure and frothing issues commonly encountered with inorganic acids during large-scale processing. Moreover, organic acids tend to cause less corrosion in industrial systems. However, their effectiveness decreases with more refractory minerals, and they are unsuitable for high-temperature applications due to their low boiling points and thermal decomposition [164]. Calcined carbonates leach faster with organic acids than raw carbonates, due to the increased reactivity of magnesium oxide [151]. The reaction between magnesite and a generic organic acid (HR) can be represented schematically as follows:

$$MgCO_{3(s)} + 2HR_{(aq)} \rightarrow MgR_2 + CO_{2(g)} + H_2O_{(l)} \quad (21)$$

In the reaction described, HR stands for an organic acid, which may be formic (HCOOH), acetic (CH_3COOH), citric ($C_6H_8O_7$), lactic ($C_3H_6O_3$), succinic ($C_4H_6O_4$), or gluconic ($C_6H_{12}O_7$) acid.

Mg extraction from silicates: The technology for large-scale magnesium recovery from Mg-bearing silicate minerals remains in the research and development stage [172]. Serpentinite, a magnesium-rich silicate mineral, presents a promising source for magnesium extraction, supporting resource conservation and environmental sustainability while enhancing economic efficiency [173,174]. Effective optimization of extraction methods from serpentine is essential, as it reduces the need for new magnesium sources and minimizes the use of energy-intensive processes. This not only offers economic benefits by lowering production costs but also contributes to environmental sustainability by reducing waste and utilizing serpentine residues for producing $Mg(OH)_2$ [175].

Serpentine minerals possess a layered structure of tetrahedral silicates and magnesium hydroxide, which imparts both stability and challenges for magnesium extraction. In this structure, silicon-centered tetrahedra share three of their four apical oxygen atoms with adjacent tetrahedra, while unshared oxygen atoms bond to magnesium in octahedral sheets. This arrangement gives serpentine its remarkable stability, complicating its decomposition in traditional hydrometallurgical processes. To address these challenges, pretreatment techniques such as thermal, mechanical, and chemical treatments have been developed to enhance the extraction of soluble magnesium. Despite their inherent resistance to both acidic and alkaline solutions due to their acid-base characteristics, these pretreatment methods significantly improve magnesium recovery, making serpentine a valuable resource for industrial magnesium production [34,176].

- ***Thermal pretreatment*:** Under ambient conditions, the leaching of magnesium from natural serpentine (Equation (22)) is limited. This step is generally considered the rate-limiting step and requires strong acidic conditions for effective magnesium recovery [177,178].

$$2Mg_3Si_2O_5(OH)_{4(s)} + 6H^+_{(aq)} \rightarrow 3Mg^{2+}_{(aq)} + 2H_2SiO_{4(aq)} + 7H_2O_{(l)} \quad (22)$$

Thermal treatment increases the reactivity of serpentine to acid leaching by removing structural hydroxyl groups and converting the mineral into an amorphous form. Heating serpentine between 800 °C and 1000 °C promotes its transformation into forsterite (Equation (23)) [179–181]. However, other researchers demonstrated that heating serpen-

tine to approximately 750 °C converts lizardite and antigorite into forsterite, silica, and an amorphous phase [182], whilst temperatures above 800 °C favor the formation of enstatite.

$$2Mg_3Si_2O_5(OH)_{4(s)} \rightarrow 3Mg_2SiO_{4(s)} + SiO_{2(s)} + 4H_2O_{(g)} \quad (23)$$

During thermal treatment, the removal of hydroxyl groups linking the brucitic and silica layers disrupts weak Mg–O bonds, thereby facilitating the release of magnesium [35]. Between 600 °C and 700 °C, serpentine is converted into a more reactive intermediate, $Mg_3Si_2O_7$ (dehydroxylate), through the loss of water (Equation (24)). At temperatures above 800 °C, this intermediate further transforms into forsterite and silica (Equation (25)) [179,182–184].

$$Mg_3Si_2O_5(OH)_{4(s)} \rightarrow Mg_3Si_2O_{7(s)} + 2H_2O_{(g)} \quad (24)$$

$$Mg_3Si_2O_{7(s)} \rightarrow 3Mg_2SiO_{4(s)} + SiO_{2(s)} \quad (25)$$

Above 1000 °C, forsterite may react with silica to form both forsterite and enstatite (Equation (26)) [179].

$$3Mg_2SiO_{4(s)} + SiO_{2(s)} \rightarrow 2Mg_2SiO_{4(s)} + Mg_2Si_2O_{6(s)} \quad (26)$$

Calcining serpentine is believed to enhance magnesium dissolution, potentially reducing leaching time, temperature, and pressure requirements [178,179]. Additionally, this thermal pretreatment can mitigate corrosion issues in leaching equipment and decrease the need for leaching agents [181].

- ***Mechanical pretreatment*:** Activates by means of physical methods the serpentine surface to improve its leachability by removing the surface layer of silica (SiO_2), which can hinder the dissolution of magnesium within the mineral. This layer of silica acts as a barrier, limiting solvent access to the mineral's interior. Techniques such as grinding, stirring, ultrasonic treatment, and microwave irradiation are applied prior to leaching to overcome this barrier [176,185–187].

Grinding reduces particle size and creates irregular surfaces, accelerating dehydration and delaying the recrystallization of reaction products, thereby postponing the formation of resistant crystalline phases such as forsterite and enstatite [188–191]. Ultrasonic treatment alters the serpentine structure without breaking its chemical bonds. This enhances water mobility and promotes more efficient water release during subsequent thermal treatment [192,193]. Microwave pretreatment further facilitates serpentine's transformation into olivine, lowers slurry viscosity, improves grindability, enhances magnesium release, and reduces overall energy consumption [194].

- ***Chemical pretreatment*:** To reduce costs and energy consumption in the leaching of layered aluminosilicates, researchers are exploring chemical activation as a cost-effective alternative to thermal and mechanical methods. One promising approach involves using additive materials such as sodium fluoride or calcium fluoride. These fluoride ions react with aluminum in hydrosilicates, aluminosilicates, and laterites to form soluble complexes. This reaction lowers the activation energy required for leaching, thereby improving magnesium dissolution [195,196].

The stable layered structure of serpentine, which hinders efficient magnesium extraction, can be disrupted by introducing fluorite powder. Fluorine ions (F^-) interact with silicon (Si) in serpentine, leading to a distorted tetrahedral arrangement that relaxes the crystal structure. This structural change exposes more magnesium and significantly enhances its recovery [195].

In the chemical treatment, structural oxygen in tetrahedra is removed by hydrogen ions (H^+), allowing fluoride ions (F^-) to bond with the exposed aluminum atoms. This interaction forms the $[AlF_4]^-$ complex, which then reacts with additional fluoride ions to produce the stable $[AlF_5]^{2-}$ in solution. The effectiveness of fluoride ions is attributed to their smaller size and higher electronegativity compared to HSO_4^- and SO_4^{2-} [196].

- ***HCl leaching*:** The recovery of magnesium from serpentine using hydrochloric acid (HCl) has been extensively studied as a method for extracting magnesium from Mg-rich silicate ores [34,159,197–202]. This process involves leaching serpentine with hydrochloric acid to produce magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$). Atmospheric chloride leaching offers several benefits, including lower capital costs, reduced reagent usage, and improved residue handling characteristics such as better settling and filtration [203].

The chemical reaction for leaching magnesium from serpentinite ore with hydrochloric acid is as follows [33,200,201]:

$$Mg_3Si_2O_5(OH)_{4(s)} + 6HCl_{(aq)} \rightarrow 3MgCl_{2(aq)} + 2SiO_{2(s)} + 5H_2O_{(l)} \quad (27)$$

In the Magnola process (Figure 4), asbestos tailings containing approximately 24% magnesium are treated with hydrochloric acid to extract the magnesium. The resulting mixture is neutralized and filtered, producing a silica–iron residue and a magnesium chloride ($MgCl_2$) brine. The brine is partially dehydrated in a spray fluidized bed dryer, producing $MgCl_2 \cdot xH_2O$ prills. These prills are then fed into a Super-Chlorinator. There, the prills are fully dehydrated, and any residual MgO reacts to form pure, oxide-free $MgCl_2$. The anhydrous $MgCl_2$ is then electrolysis in an Alcan multi-polar cell to produce metallic magnesium. The chlorine gas generated during electrolysis is recycled to regenerate HCl. This HCl is then reused in the initial leaching step, thus completing a closed-loop system for acid recovery [82,204–206].

During the leaching process, the accumulation of $MgCl_2$ in the solution can slow down the leaching rate and cause HCl to evaporate due to high chloride concentrations [197]. A study outlines a process for recovering magnesium from serpentine HCl-leaching solution through leaching, purification, and precipitation steps. This method involves synthesizing high-purity magnesium hydroxide and magnesium carbonate by precipitating magnesium chloride with 1,4-dioxane [207].

Another study reported the production of 84% pure MgO from olivine via hydrochloric acid leaching, followed by precipitation and calcination. This method efficiently removed impurities such as silica and iron, producing MgO suitable for civil engineering and CO_2 sequestration. Characterization revealed a periclase structure, with reactivity declining at higher calcination temperatures, indicating potential for process optimization to enhance purity and surface area [208].

- ***Sulfuric acid leaching*** Several studies [35,36,172,179,186,209,210] have proposed that the H_2SO_4-leaching process is an effective method for extracting magnesium from magnesium-bearing silicate minerals. The extraction of magnesium from magnesium silicates using sulfuric acid involves the following reactions [37,172,211]:

$$Mg_3Si_2O_5(OH)_{4(s)} + 3H_2SO_{4(aq)} \rightarrow 3MgSO_{4(aq)} + 2SiO_{2(s)} + 5H_2O_{(l)} \quad (28)$$

$$Mg_2SiO_{4(s)} + 2H_2SO_{4(aq)} \rightarrow 2MgSO_{4(aq)} + SiO_{2(s)} + 2H_2O_{(l)} \quad (29)$$

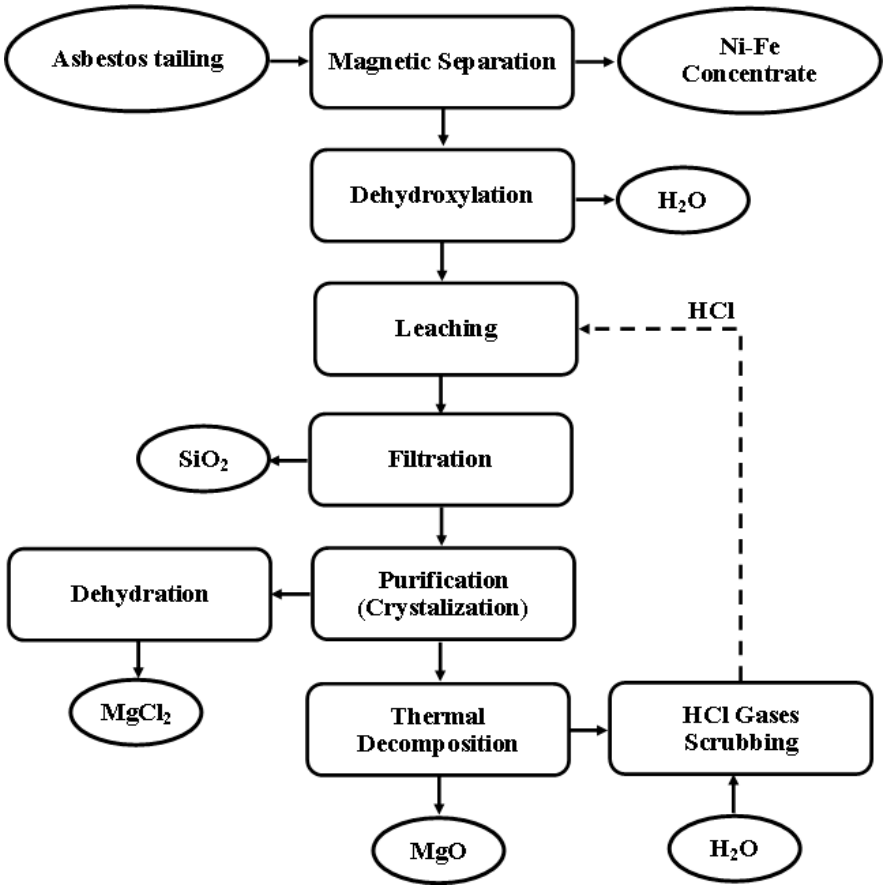

Figure 4. Magnola process flow diagram for Mg extraction from asbestos tailings [206].

Dissolving magnesium from a crystalline structure typically results in the collapse of the original ordered structure and the formation of amorphous hydrated silica. This process carves micropores between the SiO_4 tetrahedral layers which are then modified by the condensation of silanol groups within them [209].

Figure 5 shows a proposed process flow diagram for producing both hydrated and anhydrous magnesium sulfate by leaching serpentine ore with sulfuric acid [179].

Research indicates that under acidic conditions, the brucitic layers dissolve from serpentine, leaving behind microporous silica-based materials. This means that complete dissolution of serpentine is not necessary for full magnesium extraction. However, the presence of other metal ions can complicate the recovery process [172,209].

A two-step purification process was developed to obtain pure magnesium sulfate ($MgSO_4$) from sulfuric acid-leached serpentine solutions [175]. This approach involves producing high-purity magnesium hydroxide and magnesium carbonate by removing metal impurities such as iron, aluminum, chromium, manganese, nickel, and cobalt. After oxidation with H_2O_2, iron, aluminum, and chromium precipitate as metal hydroxides using MgO as the precipitant (Equation (30)). Then, Mn, Ni, and Co are removed through precipitation with Na_2S (Equation (31)).

$$(Fe, Al, Cr)_2(SO_4)_{3(aq)} + 3H_2O_{(l)} + 3MgO_{(s)} \rightarrow 2(Fe, Al, Cr)(OH)_{3(s)} + 3MgSO_{4(aq)} \quad (30)$$

$$(Mn, Ni, Co)SO_{4(aq)} + Na_2S_{(aq)} \rightarrow (Mn, Ni, Co)S_{(s)} + Na_2SO_{4(aq)} \quad (31)$$

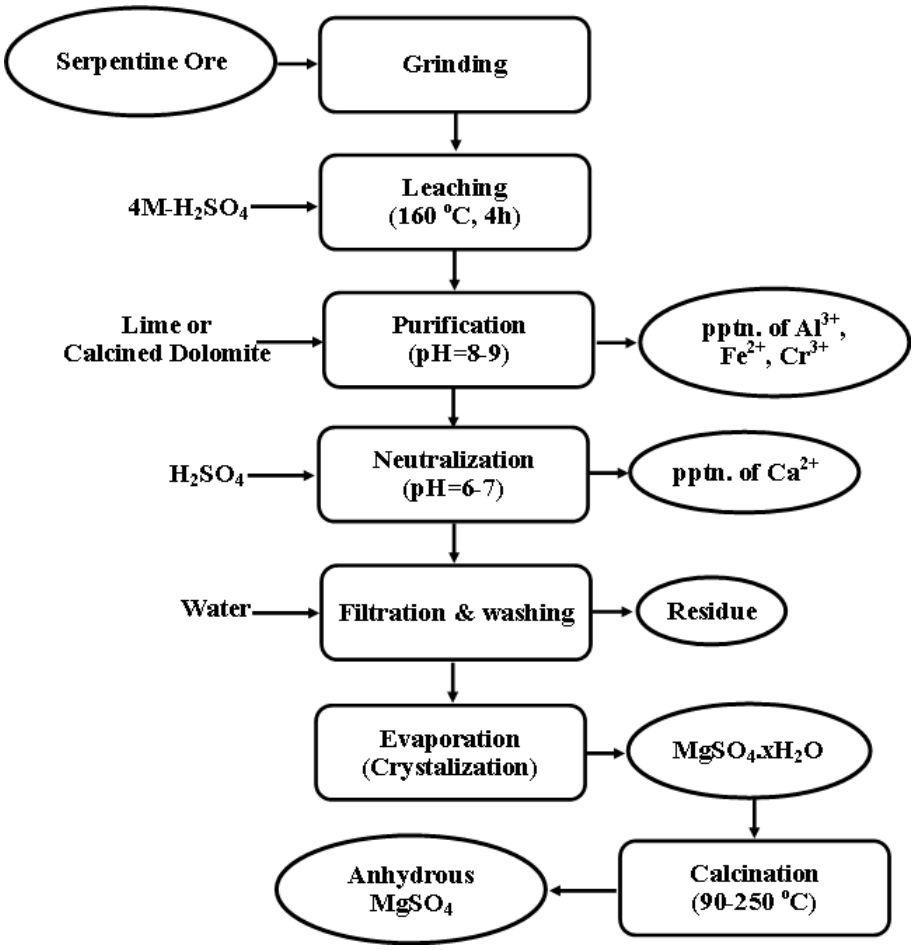

Figure 5. Production of $MgSO_4$ from serpentine leaching.

$Mg(OH)_2$ and $4MgCO_3{\cdot}Mg(OH)_2{\cdot}4H_2O$ are synthesized through a two-stage precipitation of the purified $MgSO_4$ solution. In the first stage, Mg^{2+} ions are precipitated with $NH_3{\cdot}H_2O$ to form $Mg(OH)_2$ (Equation (32)), and in the second stage, the remaining solution is treated with NH_4HCO_3 to produce $4MgCO_3{\cdot}Mg(OH)_2{\cdot}4H_2O$ (Equation (33)).

$$2NH_3{\cdot}H_2O_{(l)} + MgSO_{4(aq)} \rightarrow Mg(OH)_{2(s)} + (NH_4)_2SO_{4(aq)} \quad (32)$$

$$6NH_3 + 5MgSO_{4(aq)} + 4NH_4HCO_{3(aq)} + 6H_2O_{(l)} \rightarrow 4MgCO_3{\cdot}Mg(OH)_2{\cdot}4H_2O_{(s)} + 5(NH_4)_2SO_{4(aq)} \quad (33)$$

Several studies have also explored extracting magnesium and nickel from nickel-rich serpentine by sulfation roasting followed by water leaching [34,38].

Microwave-assisted leaching with fluorite significantly enhanced MgO and total Fe extraction from iron-bearing serpentine tailings, achieving 97.0% and 50.9% efficiencies under optimized conditions (400 W, 3 min, 70 °C, 4 mol/L H_2SO_4, 4:1 L/S ratio). Microwave pretreatment altered hematite phases, increasing reactivity with sulfuric acid and improving leaching compared to conventional methods [212].

- ***Nitric acid leaching*:** Serpentinite can be dissolved in HNO_3 solution at temperatures above 70 °C, which enhances the leaching rate with increasing temperature, as described by Equation (34) [39,213].

$$Mg_3Si_2O_5(OH)_{4(s)} + 6HNO_{3(aq)} \rightarrow 3Mg(NO_3)_{2(aq)} + 2SiO_{2(s)} + 5H_2O_{(l)} \quad (34)$$

However, leaching serpentine with nitric acid presents challenges due to the acid's oxidizing properties, which can also dissolve accompanying impurities. The dissolution rate of serpentinite in nitric acid is significantly influenced by the reaction temperature. Initially, the rate of reaction controls the process, but as temperature increases, the rate is eventually limited by the diffusion of the product layer [213].

- ***Organic acid leaching*:** The leaching of silicate minerals, particularly those in the serpentine group, has been investigated using various organic acids such as formic acid [182,214], acetic acid [39,215,216], oxalic acid [216,217], citric acid [217,218], succinic acid [216], lactic acid [214], and EDTA [217]. Research indicates that the presence of organic ligands markedly improves the dissolution rate of serpentine in mildly acidic conditions [217,218]. This is thought to be due to the adsorption of organic ligands, which form surface complexes and create precursors that detach from the mineral surface. Additionally, it is believed that a negatively charged ligand binds to positively charged hydrated Mg sites on the surface [40,218,219].

Microwave-assisted citric acid leaching efficiently extracts major and critical elements from olivine at 178 °C, achieving higher, diffusion-controlled extraction rates in shorter times compared to autoclave and conventional methods, aided by the detachment of Si-rich surface layers [220].

Studies have shown that the dissolution rate of olivine increases in the presence of a potassium hydrogen phthalate–HCl buffer and ascorbic acid within a pH range of 2–6 [40]. More pronounced effects are observed at higher pH levels. This enhanced dissolution is attributed to the formation of surface complexes by organic ligands that adsorb onto hydrated magnesium sites and promote mineral detachment. At lower pH levels, the effect of these ligands diminishes due to proton saturation. Additionally, ligand concentration influences dissolution behavior similarly to hydrogen ion concentration. Other studies have reported that the type of ligand significantly affects dissolution rates. Ethylenediaminetetraacetic acid (EDTA) demonstrates the highest efficacy, followed by phthalate and acetate [221]. The reaction order for EDTA, phthalate, and folic acid is approximately 0.5. However, the influence of ligands diminishes at lower pH values.

Leaching thermally treated Mg-bearing silicate samples with formic acid showed that specimens containing forsterite and lizardite had lower magnesium extraction, while those fully serpentinized with antigorite achieved higher magnesium extraction [182,214].

- ***Ammonium salt leaching*:** Researchers have also used ammonia and its soluble salts, such as ammonium chloride (NH_4Cl), ammonium sulfate ($(NH_4)_2SO_4$), and ammonium bisulfate (NH_4HSO_4), to dissolve magnesium from silicates [222,223]. Ammonium chloride (NH_4Cl) is an effective lixiviant for extracting magnesium from silicates because it produces a relatively pure and easily refined $MgCl_2$-rich solution. Its use is advantageous in leaching processes, as it selectively dissolves magnesium from silicates while leaving other impurities behind. Ammonia released during the process can impede mineral dissolution, so removing NH_3 is necessary for smooth reaction progress. The generated ammonia can then be utilized to precipitate magnesium hydroxide ($Mg(OH)_2$) from the $MgCl_2$-rich solution [223].

It has been reported that adding NH_4Cl enhances the dissolution of magnesium from calcined serpentinite in hydrochloric acid [38]. Another study investigated the absorption of CO_2 and the precipitation of magnesium carbonate in $MgCl_2$-NH_3-NH_4Cl solutions as a method of magnesium recovery from serpentine [224].

Magnesium can also be extracted from serpentine by leaching it with NH_4HSO_4 and $(NH_4)_2SO_4$, at approximately 95–100 °C through the following reactions [222,225–227]:

$$Mg_3Si_2O_5(OH)_{4(s)} + 6NH_4HSO_{4(aq)} \rightarrow 3MgSO_{4(aq)} + 2SiO_{2(s)} + 5H_2O_{(l)} + 3(NH_4)_2SO_{4(aq)} \quad (35)$$

$$Mg_3Si_2O_5(OH)_{4(s)} + 3(NH_4)_2SO_{4(aq)} \rightarrow 3MgSO_{4(aq)} + 2SiO_{2(s)} + 5H_2O_{(l)} + 6NH_{3(g)} \quad (36)$$

Of the various ammonium salt solutions, NH_4HSO_4 has been identified as the most effective for magnesium precipitation. Aqueous magnesium sulfate can react with NH_4CO_3 and NH_3 to form magnesium carbonate species, such as $MgCO_3{\cdot}3H_2O$ (Equation (37)) and $MgCO_3{\cdot}Mg(OH)_2{\cdot}4H_2O$ (Equation (38)). The specific product formed depends on the temperature and pressure conditions [228]. Above 100 °C, hydromagnesite ($MgCO_3{\cdot}Mg(OH)_2{\cdot}4H_2O$) converts to magnesite ($MgCO_3$) [229].

$$MgSO_{4(aq)} + NH_4HCO_{3(aq)} + NH_3{\cdot}H_2O_{(aq)} + 2H_2O_{(l)} \rightarrow MgCO_3{\cdot}3H_2O_{(s)} + (NH_4)_2SO_{4(aq)} \quad (37)$$

$$5MgCO_3{\cdot}3H_2O_{(s)} \rightarrow 4MgCO_3{\cdot}Mg(OH)_2{\cdot}4H_2O_{(s)} + 10H_2O_{(l)} + CO_{2(g)} \quad (38)$$

Prior to magnesium carbonate precipitation, the solution pH must be raised to an alkaline level by adding aqueous ammonia. This facilitates the removal of impurities, such as Fe, Al, Cr, Zn, Cu, and Mn by forming metal hydroxides. The corresponding reactions for the precipitation of divalent (M^{2+}) and trivalent (M^{3+}) metal ions as hydroxides are shown in Equation (39) and Equation (40), respectively [229].

$$M^{II}SO_{4(aq)} + 2NH_3{\cdot}H_2O_{(aq)} \rightarrow M^{II}(OH)_{2(s)} + (NH_4)_2SO_{4(aq)} \quad (39)$$

$$(M^{III})_2(SO_4)_{3(aq)} + 6NH_3{\cdot}H_2O_{(aq)} \rightarrow 2M^{III}(OH)_{3(s)} + 3(NH_4)_2SO_{4(aq)} \quad (40)$$

NH_4HSO_4 and NH_3 can be regenerated by thermally decomposing $(NH_4)_2SO_4$ as shown in Equation (41) [225]:

$$(NH_4)_2SO_{4(s)} \rightarrow NH_4HSO_{4(s)} + NH_{3(g)} \quad (41)$$

Ammonium sulfate roasting–water leaching has enabled selective Mg^{2+} recovery from chrysotile asbestos tailings, achieving 84.18% leaching and 98.87% purity while minimizing impurity extraction. $MgSO_4$ forms during roasting, whereas Fe, Al, Cr, and Ni remain as insoluble oxides. The process addresses hazardous waste management but has limited Ca^{2+} removal, and roasting is the main carbon-emission contributor [230].

***NaOH leaching*:** Concentrated NaOH solutions can be used to leach serpentine at 150 °C to separate Si-Mg, producing solid $Mg(OH)_2$ as per the reaction [149]:

$$Mg_3Si_2O_5(OH)_{4(s)} + 4NaOH_{(aq)} \rightarrow 3Mg(OH)_{2(s)} + 2Na_2SiO_{3(aq)} + H_2O_{(l)} \quad (42)$$

However, in addition to Na_2SiO_3, other soluble silicate species like $NaHSiO_3$ and H_2SiO_3 can also form in the solution, particularly at high temperatures. These species are unstable and can become colloidal over time, complicating the leaching process [149,206].

- ***CO_2 leaching*:** Direct aqueous carbonation of Mg-rich silicates such as serpentine, chrysotile, and forsterite leads to the production of magnesite [178,225,229]. This overall process is represented by the following reactions:

$$2Mg_3Si_2O_5(OH)_{4(s)} + 3CO_{2(g)} \rightarrow 3MgCO_{3(s)} + 2SiO_{2(s)} + 2H_2O_{(g)} \quad (43)$$

$$Mg_2SiO_{4(s)} + 2CO_{2(g)} \rightarrow 2MgCO_{3(s)} + SiO_{2(s)} \quad (44)$$

The efficiency of this process is greatly affected by temperature, pressure, and solution pH. These factors govern the CO_2 gas–liquid equilibrium (Equation (13)) and the formation of carbonate and bicarbonate species (Equation (14)).

Another study examined the dissolution of serpentine in weakly acidic aqueous solutions containing NH_4Cl, NaCl, sodium citrate, EDTA, sodium oxalate, and sodium acetate. Experiments were conducted at 120 °C and 20 bar of CO_2 in a batch autoclave [217]. The results revealed that sodium citrate, sodium oxalate, and EDTA significantly accelerated serpentine dissolution under mildly acidic conditions.

3.3. Electrometallurgy

Electrometallurgical magnesium extraction involves the electrolysis of molten magnesium chloride, using direct current applied in electrolytic cells (Figure 6a). This process operates most efficiently at temperatures between 655 °C and 720 °C. During electrolysis, chloride ions are oxidized to form chlorine gas at the graphite anode (Equation (45)), while magnesium ions are reduced to liquid metal at the steel cathode (Equation (46)). The overall reaction produces liquid magnesium and chlorine gas (Equation (47)). The magnesium is collected for use in downstream applications, and the chlorine gas is recycled for reuse [82,109].

$$\text{Anode} : 2Cl^- \rightarrow Cl_2 + 2e^- \quad (45)$$

$$\text{Cathode} : Mg^{2+} + 2e^- \rightarrow Mg \quad (46)$$

$$MgCl_2 \rightarrow Mg_{(\text{liquid})} + Cl_{2(\text{gas})} \quad (47)$$

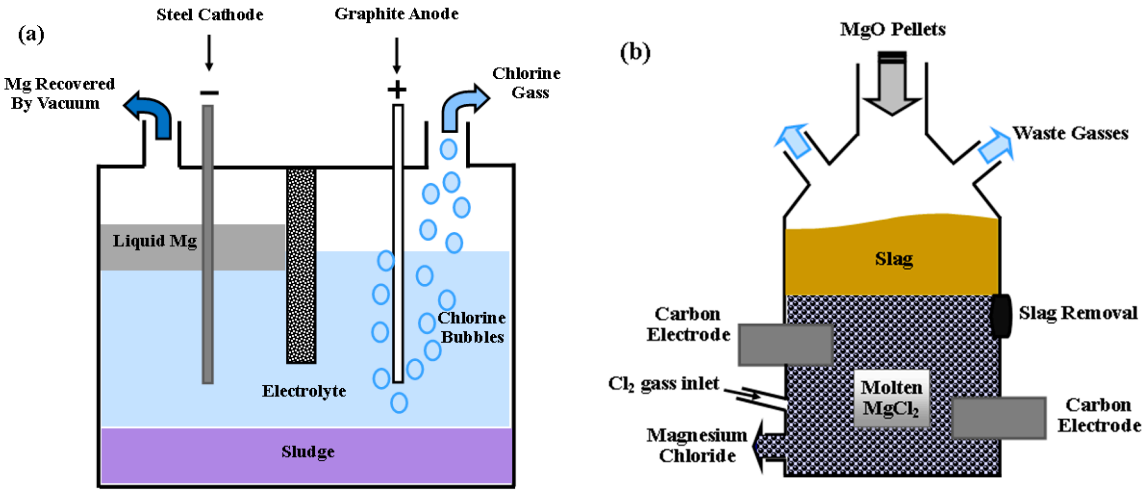

Figure 6. Electrolysis of magnesium chloride (**a**). Conversion of magnesium oxide to magnesium chloride (**b**).

Magnesium chloride can be sourced from seawater, brines, or magnesium-bearing minerals. However, the latter minerals must undergo hydrometallurgical or pyrometallurgical processing before electrolysis can produce anhydrous or partially anhydrous magnesium chloride salts.

When magnesium chloride is derived from brines, the solution undergoes impurity removal and is then concentrated through a multi-stage evaporation process. In cases where carbonate minerals are the raw material, they are first calcined at high temperatures to produce oxides (Equations (1) and (2)), which are then treated with water (Equation (48))

to precipitate magnesium hydroxide while calcium hydroxide, in the case of dolomite, remains in solution [109].

$$MgO{\cdot}CaO_{(s)} + nH_2O_{(l)} \rightarrow Mg(OH)_{2(s)} + Ca^{2+}_{(aq)} + 2(OH)^{-}_{(aq)} \quad (48)$$

The precipitated magnesium hydroxide is filtered, heated to form pure magnesium oxide, and then converted to magnesium chloride by heating the oxide with carbon in a chlorine stream at high temperatures in an electric furnace (Figure 6b and Equation (49)) [109].

$$2MgO_{(s)} + C_{(s)} + 2Cl_{2(g)} \rightarrow 2MgCl_{2(s)} + CO_{2(g)} \quad (49)$$

During this reaction, the following side reactions may also occur [109]:

$$Cl_{2(g)} + C_{(s)} + H_2O_{(g)} \rightarrow 2HCl_{(g)} + CO_{(g)} \quad (50)$$

$$2MgO_{(s)} + 2HCl_{(g)} \rightarrow MgCl_{2(s)} + H_2O_{(g)} \quad (51)$$

$$Mg(OH)Cl_{(s)} + HCl_{(g)} \rightarrow MgCl_{2(s)} + H_2O_{(g)} \quad (52)$$

Magnesium extraction methods from different mineral sources can be classified into two categories: (1) magnesium metal production processes and (2) magnesium compound production processes (Table 3).

Table 3. Categorization of magnesium extraction processes.

Category	Feedstocks	Main Processes	Products
Mg Metal Production	Magnesite Dolomite Brucite	Pidgeon process Electrolytic reduction	High-purity Mg Metal
Mg Compound Production	Seawater Brines Leaching solutions	Precipitation	MgO $Mg(OH)_2$ $MgCl_2$ $MgSO_4$

4. Conclusions and Future Research Priorities

This updated accounting highlights various methods of extracting magnesium from non-saline sources. This practice is becoming increasingly important due to the growing global demand for magnesium, an essential metal. While traditional sources, such as seawater and brines, remain significant, mineral-based alternatives—including carbonates, silicates, halides, oxides, and hydroxides—show great promise for expanding global supply. The review discusses extraction techniques such as pyrometallurgy, hydrometallurgy, and electrometallurgy, each offering unique advantages and limitations. Pyrometallurgical methods, such as silicothermic and aluminothermic reduction, are well-established but highly energy-intensive. Hydrometallurgical approaches, involving leaching with inorganic or organic acids or ammonium salts, provide greater process flexibility and potentially lower environmental impacts, though they demand precise control of reaction conditions and reagent recycling. Electrometallurgical techniques, particularly the electrolysis of magnesium chloride, are efficient on an industrial scale but require extensive upstream processing and careful impurity management. Recent advances in thermal, mechanical, and chemical activation have further improved magnesium recovery from silicate minerals. Looking forward, a strategic research roadmap is essential to bridge existing gaps and accelerate the transition toward more sustainable and economically viable magnesium extraction technologies. Key priorities include the following:

***Energy-efficient process development*:** Reducing the energy intensity of pyrometallurgical routes through process optimization, hybrid systems, or the integration of renewable energy sources.

***Green hydrometallurgy*:** Designing selective, low-cost, and recyclable leaching agents—including bioleaching or deep eutectic solvents—to minimize waste and environmental impact.

***Electrochemical advancements*:** Enhancing the efficiency of electrolysis by improving electrode materials, reducing chlorine emissions, and developing direct electrochemical reduction methods for silicate and carbonate feedstocks.

***Pretreatment and activation innovations*:** Advancing physical and chemical pretreatment techniques to unlock low-grade silicate and serpentine ores for large-scale applications.

***Process integration and circularity*:** Establishing closed-loop systems for reagent recovery, energy reuse, and by-product valorization to enhance process sustainability.

***Techno-economic and life-cycle assessments*:** Conducting rigorous analyses to identify the most cost-effective and environmentally sustainable pathways under varying resource and market conditions.

By aligning research efforts with these priorities, the industry can move toward more efficient, scalable, and environmentally responsible magnesium production pathways. Such progress will be critical for meeting the increasing global demand for magnesium in strategic sectors such as automotive, aerospace, energy storage, and environmental technologies.

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