Ethiopian International Journal of Multidisciplinary Research

pISSN:2349-5707 Volume:12,Issue 10,October-2025 eISSN:2349-5715

OBTAINING AND APPLICATION OF MAGNESIUM COMPOUNDS FROM RAW MATERIALS

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Magnesium, the eighth most abundant element in the Earth's crust and the second most abundant in the world's oceans after potassium, possesses unique properties that find wide application in various industries. Commercial magnesium compounds are widely used in chemical processing, whether in the production of paper or viscose fiber, or as a catalyst, filler, flame retardant, alkaline material, stable coating for magnetic recording media, or a purifier for wastewater or flue gases. Magnesium hydroxide is a common over-the-counter antacid and laxative. Furthermore, the branch of synthetic organic chemistry known as Grignard reactions is based on magnesium compounds. Magnesium forms stable salts with the most common anions, such as acetate, carbonate, halides, hydroxide, oxide, and sulfide, as well as with some less common ones, such as vanadates. Numerous magnesium alkyls are also known. Low density, high tensile strength, good thermal and electrical conductivity, and vibration absorption properties make magnesium and its compounds valuable in the aviation, automotive, medical, agricultural, and other industries [1-2].

In 2010, the United States accounted for approximately 53% of the demand for magnesia powders for refractories, leaving 47% for applications in agriculture, the chemical industry, construction, and the environment. While the United States and Canada dominated magnesium production in 1990, by the late 1990s, China had taken the lead in this industry [3].

Extraction of magnesium from natural sources such as seawater, brines, and mineral ores plays a strategic role. Seawater is the source of 15% of global magnesium production and holds a potential reserve of 1,900 million tons of magnesium compounds. Therefore, the economic evaluation of ore depends in part on the magnesium oxide concentration and processing methods. The profitability of ore processing depends on the magnesium oxide concentration, which requires careful analysis and selection of optimal technologies. The efficiency of processes such as solar evaporation of brines makes them relevant for large-scale magnesium production [4].

In this study, the dissolution kinetics of natural magnesite is analyzed using formic acid as a leaching agent. The effects of various reaction parameters, such as temperature, acid solution concentration, particle size, and liquid-to-solid ratio, were studied in relation to the leaching kinetics of natural magnesite [5]. The key to extracting magnesite powder is producing a high-quality product with an MgO content of 96 to 99%, high density, and microgranularity (40-80 μm), which is essential for the manufacture of refractory materials. The powder is extracted from the brine by precipitating it with calcined dolomite, and brucite is formed by the reaction:

$CaO(MgO) + MgCl_2 + 2H_2O \rightarrow 2Mg(OH)_2\downarrow + CaCl_2$ (1).

This technology has found wide application in Western Europe and the United States, as well as in Israel, China, Japan, Mexico, and Jordan [6; 200 p.]. Today, Western electrolytic process manufacturers have been replaced by Chinese pyrometallurgical plants using the Pigeon process. The method is based on the thermal reduction of magnesium oxide (MgO) from dolomite ($MgCO_3$ $CaCO_3$) using silicon as a reducing agent. This process takes place in a vacuum or at low pressure, which facilitates the evaporation of magnesium at a relatively low temperature. China has become the primary user of the Pigeon process due to the availability of cheap coal, large quantities of dolomite and ferrosilicon, and inexpensive labor. As a result, China has become the world leader in magnesium production, significantly reducing its production costs.

pISSN:2349-5707 Volume:12,Issue 10,October-2025 eISSN:2349-5715

Thus, in 2008, an Australian company estimated the value of magnesium produced using this innovative technology at $3,000 per ton [7; pp. 63-69].
These methods are primarily concentrated on the use of dolomite and magnesite, which involve thermal roasting (700–800°C) and electrolysis, as well as magnesium leaching and precipitation with lime or caustic magnesite, and fusion with ferrosilicate [8; p. 1197].
There are also methods for reducing magnesium with metallic aluminum (the aluminothermy method) [9; pp. 65-70] at 1700°C:
$MgO + Al \rightarrow Mg + MgAl_2O_4$ (1.2)
The carbothermic method is accompanied by magnesium reduction at a temperature of 1500°C [10; p. 463-473, 11; pp. 51-55]:
$MgO + C \rightarrow Mg + CO$ (1.3)
Magnesium electrolysis is a method for producing magnesium from magnesium chloride ($MgCl_2$) extracted from seawater or brines. The process occurs at approximately 700°C, where $MgCl_2$ decomposes into magnesium and chlorine under the influence of an electric current:
MgCl electrolysis Mg2+↑ + Cl2-↑
The main advantages are high magnesium purity, automation, and lower CO_2 emissions compared to thermal methods. However, the technology requires high capital investment and inexpensive electricity, so it is used in countries with readily available renewable energy, such as Canada, Iceland, and Norway. Significant reserves of magnesium salts have been discovered in the CIS countries. They are found in natural brines, potassium-magnesium basins, salt lakes, and marine sediments. In Russia, large deposits are located in the Caspian Lowland (Astrakhan Oblast), the Irkutsk and Orenburg Oblasts, and in Perm Krai (Solikamsk), where bischofite and carnallite are mined. In Kazakhstan, magnesium salts are found in the Zhanatas deposit and the Balkhash Basin. In Belarus, the Starobin deposit (Soligorsk) contains magnesium along with potassium salts. In Ukraine, sources of magnesium compounds include the Crimean salt lakes (Sasyk-Sivash, Sivash) and some deposits in the Donbas. In Uzbekistan, significant quantities of magnesium salts are found in the Tuzkan and Karakalpak lakes, and in Turkmenistan, in the Garlyk deposit. Magnesium salts are mined in the CIS both as a standalone operation and as a byproduct of potassium and sodium salt production. The resulting raw materials are used in metallurgy, the chemical industry, and agriculture. Research indicates that the largest magnesium salt reserves are located in Russia (approximately two-thirds), while Turkmenistan holds 20%, Ukraine 18.4%, and Kazakhstan only 0.2% [12; 200 p., 117].
Uzbekistan has large brine reserves, for example, in the Aral Sea region and other salt marshes. These brines, containing magnesium, sodium, and other elements, can be processed to produce various useful substances.
In Uzbekistan, brines and mixed salts from Lakes Karaumbet and Barsakelmes (Karakalpakstan) can serve as raw materials for the production of MgO and Mg(OH)2. The Geological Committee of Uzbekistan estimates Lake Karaumbet's reserves at over 700,000 tons of magnesium chloride (295,000 tons of MgO), of which 74,000 tons are brine. The Barsa-Kelmes brine contains 2,470,000 tons of magnesium chloride (1,040,000 tons of MgO) [12; 200 p.]. Overall, the total magnesium chloride reserves in the brine of these lakes exceed 3.5 million tons, equivalent to 1.1 million tons of MgO in Barsa-Kelmes and over 300,000 tons of MgO in Karaumbet. These resources are a valuable source, but the processing involves several complex stages.
An additional product of the technology is table salt (NaCl), which increases the economic efficiency of the process. However, it should be noted that this development remains at the laboratory research stage and requires further refinement and scaling up for industrial application.
In [13-16], scientists developed a two-stage evaporation method for filtered brine from Lakes Barsa-Kelmes and Karaumbet in Karakalpakstan.
Crystalline magnesite ($MgCO_3$) is formed as a result of chemical processes occurring in natural conditions, such as precipitation from solutions and high-temperature evaporation of water. Magnesite typically forms as crystals in alkaline waters rich in magnesium or in salt lakes,

pISSN:2349-5707 Volume:12,Issue 10,October-2025 eISSN:2349-5715

especially in areas with high concentrations of magnesium salts. During precipitation, magnesite can form through evaporation of water or through biochemical reactions involving microorganisms.

$CaCO_3 + MgCl_2 \rightarrow MgCO_3 + CaCl_2$ (1.4)

Magnesite crystals can also form through metasomatism, when magnesium replaces calcium in carbonate minerals such as calcite. These processes can occur in geothermal waters under changing conditions, such as changes in temperature or water chemistry. $2CaCO_3 + MgCl_2 \rightarrow CaMg(CO_3)_2 + CaCl_2$ (1.5)

Magnesite is also found in geological formations such as limestone deposits, where exchange reactions between calcium and magnesium have occurred.

$CaMg(CO_3)_2 + MgCl_2 \rightarrow 2MgCO_3 + CaCl_2$ (1.6)

Dolomites, whose reserves in Uzbekistan are considered virtually inexhaustible, can also be used as a local raw material for magnesium production. Dolomite ($CaMg(CO_3)_2$) is an important source of magnesium and is widespread in the country, particularly in carbonate rocks, sedimentary formations, and metamorphic formations. The main dolomite deposits are concentrated in mountainous regions such as the Tien Shan and Pamir-Alai, where thick layers of these rocks are found. In industry, dolomite is used not only for the production of metallic magnesium, but also in metallurgy, construction and chemical production. Dolomites of the following deposits are of industrial significance in terms of reserves: the Sherabad deposit with a CaO content of 30.0–31.5%, MgO: 21.0–22.5%, Navbahor with CaO 28.0% and MgO 25.0%, Akhangaran with CaO: 30.2–31.0%, MgO: 21.2–22.0%, Karnak with CaO 30.02% and MgO 19.36%, Ketmonchi with CaO 30.32% and MgO 19.56%, and Jahanabad with CaO 30.56% and MgO 20.41% [17; 123 p.].

Processing methods face the challenge of forming mixtures of magnesium and calcium compounds, which complicates the production of a high-purity product, as decomposition and extraction reactions often result in mixtures of magnesium and calcium compounds. For example, calcination of dolomite at high temperatures results in the formation of oxides (MgO and CaO), which are then separated (e.g., hydration of MgO to $Mg(OH)_2$). A disadvantage of this method is the high temperatures required (approximately 900–1000°C). Acid leaching dissolves both magnesium and calcium carbonates, resulting in a solution containing Mg^{2+} and Ca^{2+} ions. The process requires several stages with additional purification and separation operations.

A review of the magnesium nitrate market in recent years shows stable growth both globally and locally, including in Russia and the CIS countries. In 2023, the global magnesium nitrate market was valued at USD 770.8 million and is projected to reach USD 1.152 billion by 2030, at a CAGR of 4.1%. The main growth drivers are the growing demand for nitrogen fertilizers and their increased use in agriculture.

Magnesium nitrate is widely used in agriculture and industry in Uzbekistan, although data on production and consumption volumes is limited. In 2023, total mineral fertilizer production, including magnesium nitrate, increased by 17% to exceed 1.4 million tons, driven by the launch of new capacity and improved production efficiency.

Imports of magnesium nitrate and other magnesium compounds in Uzbekistan are limited due to limited local processing and production capacity. The CIS and East Asian countries remain the main suppliers. Meanwhile, exports from Uzbekistan are minimal, indicating a domestic market focus [https://review.uz/post/obzor-rnka-mineralnx-udobreniy-v-period-pandemii].

In 2023, imports of magnesium nitrate and other magnesium compounds to Uzbekistan amounted to approximately $3.99 million, an 8.55% decrease compared to 2022. The share of these imported products in the country's total import volume is only 0.01%, indicating their relatively low share in the structure of trade turnover. Exports of magnesium-based fertilizers, including magnesium nitrate, are growing. Uzbekistan's main export destinations include Turkmenistan (20%), Tajikistan (14.4%), and Romania (9.44%).

pISSN:2349-5707 Volume:12,Issue 10,October-2025 eISSN:2349-5715

Import prices for magnesium nitrate and similar compounds varied depending on the supplier and volume, but the average import value increased by 48% year-on-year in 2023. Average prices for exported magnesium compounds remain competitive in the Central Asian market, facilitating their active sale within the region. Uzbekistan is focusing on developing domestic production of magnesium compounds, but remains dependent on imports to meet its full range of needs. Magnesium nitrate consumers remain primarily in the agricultural sector, where it is used as a component of fertilizers, as well as in the chemical and construction industries. The primary applications of magnesium oxide (MgO) are metallurgy and construction. Of all magnesia, 65% is used in steel production, 15% in the cement industry, 7% in refractory production, and 13% in other applications. Experience shows that refractories made from pure MgO improve the efficiency of binders, as well as the reliability and productivity of steelmaking furnaces and refractories. Furthermore, MgO and Mg(OH)2 are used to produce liquid and solid magnesium fertilizers, as well as as an additive to saltpeter. MgO in the form of magnesium chloride, bischofite, is used as a raw material for the production of defoliants.

Efficient and cost-effective extraction of magnesium from natural sources and subsequent conversion into useful compounds is key to expanding the application of this valuable metal. Ongoing research and development in this area contributes to the optimization of magnesium production processes and the increased efficiency of its use in various industries. The developed technology for processing serpentinite from the Karakalpak deposit has been successfully tested at the pilot scale. It enables magnesium extraction with an efficiency of 75–86%, reducing process waste by 25% [18–19].

The basic processing flow chart includes the stages of heat treatment, nitric acid decomposition, ammoniation, and subsequent extraction of magnesium compounds. These processes have proven their effectiveness in industrial applications.

An economic analysis has shown that the proposed technology reduces production costs, creates added value through the production of multifunctional products (magnesium nitrate, iron- and aluminum-containing concentrate, and liquid fertilizers), and improves the sustainability of fertilizer production facilities.

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