

US EPA ARCHIVE DOCUMENT

MAGNESIUM AND MAGNESIA FROM BRINES

A. Commodity Summary

There are ten magnesium compound producers in the United States. Each of the facilities obtains its raw source material from either magnetite, lake brines, well brines, or seawater. In addition, there are three facilities that produce magnesium metal. Magnesia, the primary magnesium compound, is produced at three facilities. Exhibits 1 through 3 present the names and locations of facilities involved in the production of magnesium, magnesium metal, and magnesia from brines, respectively.

Magnetite and dolomite, which have a theoretical magnesium content of 47.6% and 22%, respectively, comprise the largest mineral sources of magnesium and magnesium compounds. Other sources of magnesium and its compounds include seawater, brines, and bitterns.¹

Magnesium and its alloys are used in the manufacture of structural components for automobiles, trucks, aircraft, computers, and power tools. Because of its light weight and ease of machinability, magnesium is used by the iron and steel industry for external hot-metal desulfurization and in the production of nodular iron. Producers of several nonferrous metals often use magnesium as a reducing agent. Magnesium anodes are used for cathodic protection of underground pipe and water tanks. Small quantities of magnesium are used as a catalyst in the synthesis of organic compounds, as photoengraving plates, and in alloys (other than aluminum). Caustic magnesia can be used as a cement if combined with magnesium chloride.

Refractory magnesia represents the largest use of magnesium in compounds. It is used principally for linings in furnaces and auxiliary equipment used to produce iron and steel. Caustic-calcined magnesia (partially calcined magnesite) is used in the agricultural, chemical, construction, and manufacturing industries.²

The most commonly used source for magnesia is magnesium carbonate, with the largest source being magnesia-rich brines and seawater. Magnesite is one of the minerals directly and widely exploited for its magnesia content. When pure, it contains 47.8% magnesia and 52.2% carbon dioxide. Sintered magnesia is used for refractory manufacturing while lighter fired caustic magnesia is used in fluxes, fillers, insulation, cements, decolorants, fertilizers, chemicals, in the treatment of wastewater including pH control, and in the removal of sulfur compounds from gas exhaust stacks. In addition to naturally occurring magnesia, refractory grade magnesia can also be produced synthetically. This involves the calcination of either magnesium hydroxide or magnesium chloride.³

B. Generalized Process Description

1. Discussion of Typical Production Processes

The two main operation types for recovery of magnesium are (1) electrolytic production, and (2) thermal production. Each of these processes is described in more detail below.

¹ Deborah A. Kramer, "Magnesite and Magnesia," from Minerals Yearbook Volume 1. Metals and Minerals, U.S. Bureau of Mines, 1992, pp. 163-173.

² Ibid.

³ L.R. Duncan and W.H. McCracken, "Magnesite and Magnesia," from Industrial Minerals and Rocks, 6th ed., Society for Mining, Metallurgy, and Exploration, 1994, pp. 643-654.

EXHIBIT 1

SUMMARY OF MAGNESIUM PROCESSING FACILITIES

Facility Name	Location	Type of Operations
Barcroft Co.	Lewes, DE	MgO from seawater
Dow Chemical Co.	Freeport, TX	MgCl from seawater
Great Salt Lake	Ogden, UT	MgCl from lake brine
Marine Magnesium Co.	South San Francisco, CA	MgO from seawater
Martin Marietta Chemicals	Manistee, MI	MgCl from brine
Morton Chemical Co.	Manistee, MI	MgCl from brine
National Refractories & Minerals Corp.	Moss Landing, CA	MgO from seawater
Premier Services Inc.	Port St. Joe, FL	MgO from seawater
Premier Services Inc.	Gabbs, NV	Mine magnesium carbonate and calcine to MgO
Reilly Ind.	Wendover, UT	Brine Extraction

EXHIBIT 2

SUMMARY OF MAGNESIUM METAL PROCESSING FACILITIES

Facility	Location
Dow Chemical Co.	Freeport, TX
Magnesium Corp. of America	Rowley, UT
Northwest Alloys Inc.	Addy, WA

EXHIBIT 3

SUMMARY OF MAGNESIA (MGO) PROCESSING FACILITIES

Facility Name	Location	Type of Operations
Basic Incorporated	Gabbs, NV	Uncertain
Dow Chemical Co.	Freeport, TX	Brine Extraction
Magnesia Operations	San Francisco, CA	Uncertain

2. Generalized Process Flow Diagram

Electrolytic Production

Hydrous Magnesium Chloride Feed. The Dow Chemical Company is the only magnesium producer using hydrous magnesium chloride as feed for the electrolytic cells. A flow sheet of the Dow process is presented in Exhibit 4. In this process, magnesium is precipitated from seawater as magnesium hydroxide by addition of lime or caustic in large agitated flocculators. The magnesium hydroxide is then settled in Dorr thickeners. The overflow enters the plant wastewater system where it is neutralized and returned to the ocean. The thickened underflow is pumped to rotary filters where it is dewatered, washed, and reslurried with wash water from the magnesium chloride purification step. It is then pumped to the neutralizers where it is treated with hydrochloric acid and enough sulfuric acid to precipitate excess calcium as calcium sulfate. The brine is filtered to remove calcium sulfate and other solids such as clays and silica and is further purified to reduce sulfate and boron and forwarded to the dryer. The purified brine is dried by direct contact with combustion gases in a fluid-bed dryer to produce granules of magnesium chloride. The granules are stored in large tanks from which they are fed to the electrolytic cells. The cells are fed semicontinuously and produce both magnesium and chlorine. The dilute, wet chlorine gas is drawn into refractory regenerative furnaces and converted to HCl which is recycled to neutralize magnesium hydroxide. The magnesium collects in compartments in the front of the cell from which it is periodically pumped into a computer-controlled crucible car operating at ground level. The crucible is conveyed to the casting house where it is emptied into a holding furnace or into alloying pots from which the metal is pumped into molds on continuous mold conveyors.⁴

Surface Brine Feed. A second process for magnesium production, shown in Exhibit 5, utilizes surface brine from the Great Salt Lake as feed to a series of solar evaporation ponds. This brine is further concentrated and treated with CaCl_2 . Solids such as calcium sulfate and potassium and sodium chlorides are removed in a thickener. Further concentration provides feed for the spray dryer whose waste gases provide heat for the concentration process. The spray dryers convert the brine into a dry MgCl_2 powder containing about 4% magnesia, 4% water, and other salts which comprise the cell bath. The dryers are heated with exhaust gases from gas-fired turbines that generated some of the power used to operate the cells. The spray-dried MgCl_2 powder is melted in large reactors and further purified with chlorine and other reactants to remove magnesium oxide, water, bromine, residual sulfate, and heavy metals. The molten MgCl_2 is then fed to the electrolytic cells. Only a part of the chlorine produced is required for chlorination, leaving up to 1kg/kg magnesium produced available for sale as byproduct chlorine.⁵

Underground Brine Feed. A third process for magnesium recovery uses underground brines as its source of raw material. Brine is pumped from below the ground into a large system of plastic-lined solar evaporation ponds, where the magnesium chloride concentration is increased to 25% which reduces the solubility of sodium chloride to 1%. The brine is then moved by pipeline to the plant where it is further concentrated, purified, and spray dried. The spray-dried feed is further purified by chlorination. The magnesium chloride is electrolyzed in diaphragmless cells and the molten magnesium is removed by vacuum ladle. It is then transported to a refining furnace where it is cast into ingots. The chlorine is collected, cleaned, and liquefied.⁶ Exhibit 5 presents a flow diagram of the process for recovering magnesium from underground brines and surface brines.

⁴ Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed., Vol. XIV, 1981, pp. 576-586, 631-635.

⁵ Ibid.

⁶ Ibid.

EXHIBIT 4

ELECTROLYTIC PRODUCTION USING HYDROUS MAGNESIUM CHLORIDE FEED

Graphic Not Available.

Source: Kirk-Othmer Encyclopedia of Chemical Technology, 1981, pp. 578.

EXHIBIT 5

ELECTROLYTIC PRODUCTION USING SURFACE BRINES AND UNDERGROUND BRINES AS FEED

Graphic Not Available.

Source: Kirk-Othmer Encyclopedia of Chemical Technology, 1981, pp. 582.

Thermal Reduction

In the thermal reduction process, magnesium oxide, as a component of calcined dolomite, reacts with a metal such as silicon to produce magnesium. The silicon is usually alloyed with iron. There are two principle methods: (1) carbothermic, and (2) silicothermic.

In the *carbothermic process*, magnesium oxide is reduced with carbon using modified shock cooling to produce magnesium and carbon monoxide. Both products are in the vapor phase. In order to recover the magnesium, the temperature must be dropped rapidly to prevent reversion. Shock cooling produces very finely divided magnesium dust which is pyrophoric.⁷

The *silicothermic process* is based on the reaction of silica with carbon to give silicon metal which is subsequently used to produce magnesium by reaction with calcined dolomite. The Pidgeon and Magnetherm processes employ this procedure.

The Pidgeon process is a batch process in which dolime and silicon are sized, briquetted, and charged into gas-fired or electrically heated retorts of nickel-chrome-steel alloy. The retort is equipped with removable baffles and a condensing section that extends from the furnace and is water-cooled. High purity crowns are remelted and cast into ingots.⁸ Exhibit 6 presents a flow diagram of the Pidgeon process.

In the Magnetherm process, sufficient alumina is added to melt the dicalcium silicate slag that forms at around 1500° C. This permits the reactor to be heated by the electrical resistance of the slag and further allows the reaction products to be removed in the molten state. About 0.45 kg calcined bauxite or alumina, 2.7 kg dolime, and 0.45 kg ferrosilicon are required to produce 0.45 kg metallic magnesium. As the reactants are fed to the furnace, magnesium is evolved and passes through a large tuyere into the condensation chamber. Magnesium collects as a liquid and runs down into a collection pot where it solidifies. The slag is tapped twice a day by introducing argon into the furnace to break the vacuum. The slag outlet is electrically lanced and the molten calcium aluminum silicate is quenched in water to stabilize the slag (which can be used as cement). About 5.9 kg slag are produced per kg magnesium. The residual ferrosilicon containing 20% silicon is removed and can be used as low grade silicon alloy. The magnesium collection crucible is removed once a day and the magnesium is remelted, alloyed if required, and then cast into ingots.⁹

Magnesia from Brines

Magnesia, magnesium oxide, is usually produced by calcining the mineral magnesite or magnesium hydroxide obtained from seawater or brine by liming. It is also produced by the thermal decomposition of magnesium chloride, magnesium sulfate, magnesium sulfite, nesquehonite, and the basic carbonate.¹⁰ A flow diagram of magnesia recovery from seawater is presented in Exhibit 7.

Magnesite ores contain varying amounts of silica, iron oxide, alumina, and lime as silicates, carbonates, and oxides. The deposits are mined selectively and the ores are often beneficiated to reduce lime and silica concentrations prior to calcining. Beneficiation methods include crushing and size

⁷ Ibid.

⁸ Ibid.

⁹ Ibid.

¹⁰ Ibid.

EXHIBIT 6
THE PIDGEON PROCESS

Graphic Not Available.

Source: Kirk-Othmer Encyclopedia of Chemical Technology, 1981, pp. 584.

EXHIBIT 7

MAGNESIA RECOVERY FROM SEAWATER

Graphic Not Available.

Source: Kirk-Othmer Encyclopedia of Chemical Technology, 1981, pp. 634.

separation, heavy-media separation, and froth flotation. Magnetic separation reduces iron concentration, but is effective only when the iron is present in the form of discrete ferromagnetic minerals rather than as ferrous carbonate.¹¹

In chemical beneficiation processes, the magnesium is dissolved as a salt, the insoluble impurities are removed by filtration or sedimentation, and purified magnesia is recovered by thermally decomposing the clean salt solution. Special processes are needed to separate out calcium due to its similarity to magnesium. Three of these processes are discussed below.

The first process to separate out calcium is the Pattinson process. In this process, a suspension of magnesium hydroxide is carbonated to form a solution of magnesium bicarbonate. After the insoluble impurities are separated, the solution is decarbonated by heating or aeration and the magnesium carbonate precipitates as the trihydrate, the pentahydrate or the basic carbonate. The precipitate is recovered from the solution by filtration or sedimentation and converted to the oxide by thermal decomposition. The highly reactive grades of caustic-calcined magnesia are usually produced using a modified form of this process.¹²

In a second process for the separation of calcium impurities, magnesium is dissolved with the aid of sulfur dioxide or a mixture of sulfur dioxide and carbon. One variation of this method can be employed to remove SO₂ from flue gas. The flue gas is treated with a magnesium hydroxide slurry in a venturi scrubber to form MgSO₃ and some MgSO₄, which is subsequently calcined to recover the magnesium oxide and sulfur dioxide. The magnesium oxide is recycled and the sulfur dioxide may be used to manufacture sulfuric acid.¹³

In a third process, magnesia is dissolved in hydrochloric acid. After the insoluble impurities are removed, the magnesium chloride solution is thermally decomposed to recover the magnesia.¹⁴

There are several operations used to recover magnesium oxide from dolomite. Because calcite and magnesite decompose at different temperatures, a stepwise decomposition permits a selective calcination in which the magnesium carbonate is completely decomposed without decomposing the calcium carbonate. The magnesium oxide is then separated mechanically from the half-calcined dolomite by screening or air separation. Another scheme employs a modification of the Pattinson process in which the dolomite is calcined, slaked, and then carbonated in steps to precipitate calcium carbonate and magnesium carbonate trihydrate. This is further carbonated to dissolve the trihydrate as magnesium bicarbonate and the calcium carbonate is removed by filtration. The clean solution is finally decarbonated to precipitate magnesium carbonate trihydrate which is thermally decomposed to produce magnesia.¹⁵

Highly reactive grades of caustic-calcined magnesia are produced by calcining basic magnesium carbonate or magnesium carbonate trihydrate in small batches under carefully controlled conditions. They generally have magnesia contents above 99% and contain small quantities of carbon dioxide and moisture. The carbonates for these grades are prepared by a variation of the Pattinson process described above. The less reactive grades are obtained by calcining magnesium hydroxide or magnesite in multiple-hearth furnaces or rotary kilns.¹⁶

Dead-burned magnesia is used almost exclusively for refractory applications in the form of basic granular refractories and brick. It is produced in a number of grades.¹⁷

Fused magnesia is produced by melting calcined magnesia in an electric arc furnace. The furnaces have water-cooled shells and no refractory linings. The material serves as its own refractory because only a small pool of material in the center is actually melted. When magnesia is fused for the purpose of making grain, it is allowed to cool in the furnace

¹¹ Ibid.

¹² Ibid.

¹³ Ibid.

¹⁴ Ibid.

¹⁵ Ibid.

¹⁶ Ibid.

¹⁷ Ibid.

after the electrodes have been removed. After cooling, it is removed from the furnace, separated from the unfused material, and crushed.¹⁸

3. Identification/Discussion of Novel (or otherwise distinct) Process(es)

None identified.

4. Beneficiation/Processing Boundaries

EPA established the criteria for determining which wastes arising from the various mineral production sectors come from mineral processing operations and which are from beneficiation activities in the September 1989 final rule (see 54 Fed. Reg. 36592, 36616 codified at 261.4(b)(7)). In essence, beneficiation operations typically serve to separate and concentrate the mineral values from waste material, remove impurities, or prepare the ore for further refinement. Beneficiation activities generally do not change the mineral values themselves other than by reducing (e.g., crushing or grinding), or enlarging (e.g., pelletizing or briquetting) particle size to facilitate processing. A chemical change in the mineral value does not typically occur in beneficiation.

Mineral processing operations, in contrast, generally follow beneficiation and serve to change the concentrated mineral value into a more useful chemical form. This is often done by using heat (e.g., smelting) or chemical reactions (e.g., acid digestion, chlorination) to change the chemical composition of the mineral. In contrast to beneficiation operations, processing activities often destroy the physical and chemical structure of the incoming ore or mineral feedstock such that the materials leaving the operation do not closely resemble those that entered the operation. Typically, beneficiation wastes are earthen in character, whereas mineral processing wastes are derived from melting or chemical changes.

EPA approached the problem of determining which operations are beneficiation and which (if any) are processing in a step-wise fashion, beginning with relatively straightforward questions and proceeding into more detailed examination of unit operations, as necessary. To locate the beneficiation/processing "line" at a given facility within this mineral commodity sector, EPA reviewed the detailed process flow diagram(s), as well as information on ore type(s), the functional importance of each step in the production sequence, and waste generation points and quantities presented above in Section B.

Electrolytic Production of Magnesium

EPA determined that for the production of magnesium through this process, the beneficiation/processing line occurs when the dried $MgCl_2$ undergoes electrolytic refining at the electrolytic magnesium cells and chlorine is chemically removed to yield pure magnesium. Therefore, because EPA has determined that all operations following the initial "processing" step in the production sequence are also considered processing operations, irrespective of whether they involve only techniques otherwise defined as beneficiation, all solid wastes arising from any such operation(s) after the initial mineral processing operation are considered mineral processing wastes, rather than beneficiation wastes. EPA presents below the mineral processing waste streams generated after the beneficiation/processing line, along with associated information on waste generation rates, characteristics, and management practices for each of these waste streams.

Production of Magnesium Through Thermal Reduction

EPA determined that in the production of magnesium through thermal reduction, the beneficiation/processing line is crossed when calcined dolomite ferrosilicon (CDF) pellets are introduced to the furnace for retorting when magnesium crystals are produced through the thermal destruction of the CDF pellets. Therefore, because EPA has determined that all operations following the initial "processing" step in the production sequence are also considered processing operations, irrespective of whether they involve only techniques otherwise defined as beneficiation, all solid wastes arising from any such operation(s) after the initial mineral processing operation are considered mineral processing wastes, rather than beneficiation wastes. EPA presents below the mineral processing waste streams generated after the beneficiation/processing line, along with associated information on waste generation rates, characteristics, and management practices for each of these waste streams.

Magnesia from Brines

EPA determined that for the production of magnesia from brines, the beneficiation/processing line occurs between filtration or sedimentation and when trihydrates are converted to the oxide through thermal decomposition. Therefore, because EPA has determined that all operations following the initial "processing" step in the production

¹⁸ Ibid.

sequence are also considered processing operations, irrespective of whether they involve only techniques otherwise defined as beneficiation, all solid wastes arising from any such operation(s) after the initial mineral processing operation are considered mineral processing wastes, rather than beneficiation wastes. EPA presents below the mineral processing waste streams generated after the beneficiation/processing line, along with associated information on waste generation rates, characteristics, and management practices for each of these waste streams.

C. Process Waste Streams

1. Extraction/Beneficiation Wastes

Ore Extraction and Beneficiation

Possible waste streams from ore extraction processes include **tailings** and **offgases** from calcining.

Brine Extraction and Beneficiation

Extraction waste streams from brines include **calcium sludge**, **spent seawater**, and **offgases**.

2. Mineral Processing Wastes

Electrolytic Production

Casting plant slag. This waste stream was generated at a rate of 3,000 metric tons per year in 1991.¹⁹ Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

Smut (sludge and dross). This waste, generated at a rate of 26,000 metric tons per year, may be toxic for barium.²⁰ Management for this waste includes disposal in an unlined surface impoundment.²¹ Waste characterization data are presented Attachment 1. This waste may be recycled and is classified as a byproduct.

Process wastewater is a possible waste stream from magnesium production. This waste was generated at a rate of 2,465,000 metric tons per year in 1991.²² Process wastewater may contain calcium sulfate and boron and have a low pH. This waste is may be discharged to a waste pond.²³ Process wastewater is a RCRA special waste.

Thermal Reduction

Cathode scrubber liquor. Dissociation of magnesium chloride molten salt from magnesium produces chlorine gas which is passed through a scrubber system. This produces a cathode scrubber liquor, which is discharged to surface impoundments with other wastewaters.²⁴ Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

¹⁹ U.S. Environmental Protection Agency, Newly Identified Mineral Processing Waste Characterization Data Set, Office of Solid Waste, Vol. I, August, 1992, pp. I-2 - I-8.

²⁰ Ibid.

²¹ U.S. Environmental Protection Agency, Technical Background Document, Development of Cost, Economic, and Small Business Impacts Arising from the Reinterpretation of the Bevill Exclusion for Mineral Processing Wastes, August 1989, pp. 3-4--3-6.

²² U.S. Environmental Protection Agency, Op. Cit., Vol. I, August, 1992, pp. I-2 - I-8.

²³ U.S. Environmental Protection Agency. Mineral Processing Waste Sampling Survey Trip Reports. AMAX Magnesium Company, Rowley, Utah. August 30, 1989.

²⁴ Ibid.

APC Dust/Sludge is a possible waste stream from magnesium production.²⁵ Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

Slag is a possible waste stream from magnesium production. Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

Casthouse dust. During the refining of magnesium metal, casthouse dust is produced. Although no published information regarding waste generation rate or characteristics was found, we used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate of 76 metric tons/yr, 760 metric tons/yr, and 7,600 metric tons, respectively. We used best engineering judgement to determine that this waste may exhibit the characteristic of toxicity for barium. This waste may be recycled and is classified as a sludge.

Magnesia from Brines

Possible waste streams from magnesia production from brines include **calciner offgases, calcium sludge,** and **spent brines** (which may be sold). Existing data and engineering judgement suggest that these materials do not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate these materials further.

D. Ancillary Hazardous Wastes

Ancillary hazardous wastes may be generated at on-site laboratories, and may include used chemicals and liquid samples. Other hazardous wastes may include spent solvents (e.g., petroleum naphtha), acidic tank cleaning wastes, and polychlorinated biphenyls from electrical transformers and capacitors. Non-hazardous wastes may include tires from trucks and large machinery, sanitary sewage, and waste oil (which may or not be hazardous) and other lubricants.

²⁵ U.S. Environmental Protection Agency, 1992, Op. Cit., pp. I-2 - I-8.

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