HISTORY OF MAGNESIUM PRODUCTION

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ABSTRACT

Electrolytic magnesium production has been the major method used to produce magnesium metal since Davy discovered magnesium in 1808. Many of the early workers developed small advances until the electrolysis of anhydrous magnesium chloride became the standard method of production. From the very first days, the importance of fully anhydrous magnesium chloride has been recognized. To this day, it remains the major problem area of economic and efficient electrolytic magnesium production.

Over the past 20 years, there has been increasing interest in using magnesium to produce lighter weight cars. Magnesium is continuing to be investigated for use in many areas. Originally, the main search was for die-cast parts. Today, all methods of fabrication are being considered, including rolling and stamping, as well as extrusions. The future of magnesium in automotive usage is expected to continue to grow at a rapid pace. Worldwide automakers are striving for better fuel economy with reduced emissions. Uses of magnesium in die-castings are projected to grow at a rate of 10%-15% per year for the next 10 years.

Magnesium prices have traditionally been too high to guarantee the economic use of the metal when competing with aluminum. The cost of magnesium and its alloys is constantly compared to aluminum by automakers on all continents. Aluminum is 50% heavier than magnesium. This means that for the same casting, a kg of aluminum alloy will make two castings, while a kg of magnesium would make three castings. Automakers have used this density relationship to compare the prices. To be fully competitive, magnesium should be priced at no more than 1.5 times the price of aluminum. This ratio only uses density and not the other advantages of magnesium such as damping capacity, dent resistance, strength, and rigidity as comparisons.

Thermal magnesium, long thought to be an uneconomical process for magnesium is being used in China. Through process improvements and the use of large amounts of low-cost labor, the selling price of magnesium is below that of aluminum on a kg-for-kg basis. This has given the automakers a brief glimpse of magnesium as a very competitive material. New electrolytic projects are being discussed that project very low costs of production.

In recent years, the interest in magnesium has increased throughout the world. There is a great deal of research and pilot plant work being done. There is more technical brainpower being applied to magnesium than ever before at anytime in history. These papers will review the efforts and projects in primary production in all areas of the world, including the CIS and PRC. The author will supply pictures, details of production or research efforts, and the status of all magnesium projects, both old and new, thermal or electrolytic.

THE MEN WHO MADE IT HAPPEN

In this exploration of magnesium history, the focus will be on the men involved. These men were not well educated in terms of today's educational requirements. Most were self-educated in the development of the

technologies and their strong beliefs were honed by constant thought and practice. Their reward was primarily scientific progress and not necessarily material reward.

Discovery of Magnesium Compounds

In 1701, M. B. Valentine prepared heavy magnesium carbonate from mother liquors obtained in the manufacture of potassium nitrate. Magnesia was confused with lime until 1754 when J. Black showed that the two substances were entirely different. Deposits of natural magnesium carbonate were discovered in Moravia in 1803 and were described by C. F. Ludwig as 'talcum carbonatum'. The term 'magnesite' was first restricted to the natural carbonate in 1808 by Dr. L. G. Karsten and was generally accepted gradually although the term 'globertite' was used in France for some time thereafter.

Sir Humphrey Davy (December 17, 1778 – May 29, 1829)

Sir Humphrey Davy is credited with the discovery of magnesium in 1808. Davy was an English chemist who was the first person to apply electrical current to isolate the alkali metals. He was born in Penzance, Cornwall, the son of a woodcarver. He was not a good student, his interest in the outdoor life being too commanding. His love of fishing continued until the end of his life. He first became interested in science in 1797 when he read some writings of Lavoisier and Nicholson.

After receiving a grammar school education, he was apprenticed to a surgeon and began medical studies, turning to chemistry in 1797 after experimentation in the offices of the physician with whom he was studying. The experiments came to the attention of Davies Gilbert, president of the Royal Society. Under Gilbert's sponsorship, in 1798, at the age of 20, Davy was appointed Superintendent of the Medical Pneumatic Institution, established in Bristol by Dr. Thomas Beddoes to study the physiological effects of new gases. In 1799, Beddoes published two papers on the work that Davy was doing. In spite of the fact that the conclusions in the first two papers were refuted, much publicity came to the Institution and to Davy. Later that year, Davy discovered and reported on the anesthetic properties of nitrous oxide (laughing gas). He suggested that it could be used in dental practice. It took nearly 50 years before the gas was tried in anesthesia.

In 1801 Davy was appointed to the newly established Royal Institution as an assistant lecturer under Count Rumford, and in 1802 advanced to professor. As a lecturer, Davy achieved a performance and presentation that could be envied by modern-day stage performers, much less college professors. History tells us that his chemical lessons and demonstrations were brilliantly presented. It was through these lectures that he first met Michael Faraday. Davy also wrote a book on agricultural chemistry and, presently, the first systematic geology course to be offered in England. His first Bakerian lecture on his experimentation on Galvinism in 1802 won the Medal of the French Institute from Napoleon, even though France and England were at war at that time.

Davy started experiments to produce metallic materials from a number of alkaline earth materials. During this work, it has been said that he laid the foundations for the world's lightest metal industry within the space of little more than a year. In 1807, he treated clay with sulfuric acid and found that reaction produced an unknown metal. He called it aluminum. He was unable to separate the new metal from oxygen in the air so he called the compound alumina. Davy started investigating the use of electricity by using a number of electrical cells in series to create a high-power battery. He passed current from the battery through water and found that he could dissociate water into hydrogen and oxygen. When he tried the same technique with a solution of potash, he still got hydrogen and oxygen. When he substituted solid potash, moistened to conduct current, he obtained fusion and isolated potassium for the first time. He quickly followed this by repeating the process and isolating sodium. After many unsuccessful attempts to use his developed procedure to isolate other alkaline metals, he altered his experimentation and followed a suggestion contained in a letter from Berzelius and Pontin. Davy succeeded in producing an amalgam of calcium, barium, strontium, and magnesium, and isolating the metals by driving off the mercury. As in the case of the alkali metals, he named the alkaline-earth metals after their oxides baryta, strontia, chalk, and magnesia, calling them Barium, Strontium, Calcium, and Magnium (at the time the word 'magnesium' was used to denote manganese).

Davy's technique consisted in mixing moistened alkaline-earth-oxide with cinnabar (mercuric sulfide) and placing the resultant paste on a platinum plate. A hollow was made in the paste to receive a drop of mercury, the whole was covered with naphtha and the platinum plate and the drop of mercury connected to the poles of the voltaic pile. The amalgam, which formed on the mercury pole, was transferred to a glass tube and the mercury distilled off. Davy gave the following description of the characteristics of magnesium:

"The metal from magnesia appears to react with the glass, especially before all the mercury has distilled off. In one experiment, in which I interrupted the distillation before the mercury had been completely removed, the metal appeared as a solid body, which exhibited the same white color and the same luster as the other metals of the alkalide-earths. It immediately sank to the bottom of the water although surrounded by gas bubbles, formed magnesia. It changed quickly in the atmosphere, a white crust forming, and finally it disintegrated into a white powder, which proved to be magnesia."

Davy later showed that oxygen could not be removed from the substance known as oxymuriatic acid and proved this substance to be an element, which he called chlorine. Davy became ill and resigned from the Royal Institution in 1812. One wonders about his veracity of his illness when we find he delivered a farewell lecture, married a wealthy widow, was knighted, and then traveled on the continent for two years taking with him his wife and assistant, Michael Faraday. Davy was known to have remarked more than once that the greatest discovery he ever made was Michael Faraday.

Michael Faraday (September 22, 1791 – August 25, 1867)

Faraday was the son of a blacksmith that was apprenticed as a bookbinder. He had a voracious appetite for the printed word, reading all the books that were brought in for binding. He was especially stimulated and challenged by technical manuscripts. After completing his apprenticeship, Faraday became a journeyman bookbinder and worked in this trade until 1813. He impressed Davy and was appointed assistant in the laboratory of the Royal Institution of Great Britain. Faraday and Davy traveled extensively in Europe during 1813-1815. It was during this period that he may have met Bunsen.

The milestones set by Faraday are monumental in the history of chemistry. At one point in time under the tutelage of Davy Faraday was a major mover in the development of the user of electricity and chemistry of the science of electrochemistry. The Laws of Electrochemistry are called Faraday's Laws. It is the law that establishes that 1000 Amperes of current passing for one hour will release one pound of magnesium. [Note: the actual law says that the amount of electricity that must be passed through an electrolyte in order to deposit (at the anode or cathode) or dissolve (from the anode) 1 gram equivalent of any substance is 96,500 ampereseconds or coulombs: the quantity of electricity is called a faraday.]

Magnesium was first isolated in 1828 by the French chemist, H. Bussy. Actually, Bussy developed a method for producing dehydrated magnesium chloride by adding chlorine to an intimate mixture of starch and magnesium oxide at elevated temperatures. The principle is the same as in use today although the starch is replaced by active carbon or carbon monoxide. Bussy is not remembered for his chloride process, but for adding potassium to the melt and thus directly the first metallic magnesium in a metallothermic process.

Faraday produced magnesium in 1833 by electrolysis of fused anhydrous magnesium chloride.

EARLY HISTORY OF MAGNESIUM METAL (1808-1909)

Magnesium was discovered about the same time as aluminum. Sir Humphrey Davy, the great British [Cornish] chemist, first isolated aluminum in 1807 and identified magnesium in 1808. Davy discovered many metals and other processes, however he always said his greatest discovery was Michael Faraday. Faraday produced magnesium metal by electrolysis of fused anhydrous magnesium chloride in 1833. Commercial production of magnesium by electrolysis is credited to Robert Bunsen, the German scientist, who made a small laboratory cell for the electrolysis of fused magnesium chloride in 1852.

Commercial electrolytic magnesium began in Germany in 1886, by using a modification of Bunsen's cell. The Aluminium und Magnesium Farbik, Hemelingen (Germany) designed and built a plant for the dehydration and electrolysis of molten carnallite. In 1896, this process was further developed by Chemische Fabrik Griesheim-Elektron, who transferred the process to its Bitterfeld Works and became the only magnesium producer in the world until 1916. Griesheim-Elektron became part of the I.G. Farbenindustrie.

WORLD WAR I INCREASED MAGNESIUM INTEREST

The history of magnesium from a curiosity metal to an industrial material was greatly affected by wars. While the Germans were developing magnesium production and uses in the early 1900, they also were spurred along by the need for magnesium in the military.

In 1915, the effects of World War I caused a shortage of magnesium metal, powder for flares and tracer bullets. The price of the product was \$2.20 to \$2.70 per kg. Eight companies in North America went into the production of magnesium metal. General Electric built the first magnesium plant in the United States in 1914 at Schenectady, New York. The military requirements for World War I stepped up total world production to an estimated 3,000 tons per year. Immediately after the war, the production dropped to less than 400 tons per year. As soon as the war ended in 1918, the number of companies dropped off to two in the U.S., Dow Chemical and Alcoa's American Magnesium Corporation. Dow researchers developed a special electrolytic process using a "wet" feed, 72% magnesium chloride (MgCl₂•1.5H₂O). Dow fed the "wet" material into a specially designed cell that required continual replacement of the carbon electrodes. This eliminated the problem of getting fully anhydrous magnesium chloride, but it produced an operation that required a higher level of manpower to tend the cells on a daily basis.

American Magnesium Corporation (1920-1928) used the modification of the aluminum electrolysis process, which had been developed by Harvey (1). A large steel cell was filled with a molten bath of fluoride material and magnesium oxide was dissolved in this bath and electrolyzed to produce magnesium metal with oxygen as a byproduct. The reaction temperature was 900-1000 °C. While current efficiencies were 50%, the energy efficiency was 10%.

In Britain, in 1914, Johnson, Matthey and Co. and Vickers, built a magnesium production plant using the sodium reduction of fused anhydrous magnesium chloride. This plant made magnesium powder, wire, and ribbon required for pyrotechnics. The plant was closed in 1920.

In late 1915, French Societe d'Electrochimie built a magnesium plant at Clavaux, Isere, which extracted magnesium from magnesium chloride by the electrolytic process. In 1916, the plant produced 25 metric tons. In 1922, the Compagnie Alais, Proges et Carmargue, now Pechiney, erected a similar plant at Epierre, in Savoie.

In Canada, magnesium was made by Shawinigan Electro-Metals Company at Shawinigan Falls, Ontario in 1915. In 1918, the plant was the largest producer in North America with a daily output of 300-400 kg per day. The plant operated until 1919 and was closed down. (2)

The Russian technical and mining community was investigating and working to develop the potassiummagnesium salts that were located in the Perm region near Solikamsk. All new kinds of military uses for magnesium were becoming known. In 1915, the specialists of the Petrograd Electro-Chemical Institute went to work on a project commissioned by the South Ural joint stock company, Magnesite, to extract magnesium from magnesite. The technical team quickly realized that the carnallite, also available in the same area, was a more appropriate material. Several kilograms of magnesium were produced in 1914-1915 at Petrograd Polytechnical Institute. It is recognized that the founder of magnesium metallurgy in Russia and of a national school of electrochemists was Pavel Pavlovich Fedotyev. (3)

Total annual wartime production of magnesium for all countries may have reached 3,000-5,000 metric tons. After the war, the production quickly dropped off as many of the wartime subsidized producing companies left the business.

BETWEEN THE WARS

When the wartime requirements stopped, the ability to produce magnesium and sell at a profit also stopped for many of the newer companies in all countries. So they closed and went out of business.

Most magnesium was used in pyrotechnics until the basic problems associated with producing castings (and other fabrications) were overcome. The property that made magnesium attractive for flares and tracer bullets created great problems in the foundry. Magnesium tends to oxidize readily when molten. Hence, the melting of magnesium alloys in an open crucible caused burning on the surface of the molten metal and the oxides formed would become inclusions in the sand castings made from the metal dipped from the crucible. Sand castings used water to bond the sand and this water would react with the magnesium giving burnt spots on the casting surfaces.

A German magnesium research group working at Bitterfeld discovered that carnallite salts could protect the surface of the melting magnesium (4). This cover flux also gave a refining action when stirred into the melt. Fused salt flux mixtures were designed and used to absorb the oxides, nitrides, and chlorides. This step was discovered in 1925 and it gave a process to produce very high-quality castings without inclusions (entrapped foreign particles). Sulfur and other chemicals were added to the sand to suppress the reaction with the moisture in the sand. Actual development of usable sand castings expanded commercially in the early 1920 period. After a long slow introduction, the use of magnesium in structural areas started as castings and grew to forging, extrusions, and rolled products, mostly in Germany. The development of magnesium use did not expand rapidly until the military build up of World War II started and new areas of use continued through the war.

The magnesium industry in the United States consisted of Dow Chemical alone from 1928 until 1940. While Germany and Japan were building up their magnesium industries in the 1930's, the U.S. and Canada were running pilot plants and looking at new technology. Henry J. Kaiser, the noted American industrialist was building a carbothermic magnesium plant in California. The plant used seawater magnesia (MgO) and coke as a reductant. Dow continued to operate their original electrolytic magnesium plant in Midland, Michigan. This plant used brine for the feedstock. In 1940, Dow also built a plant to produce magnesium from seawater in Freeport, Texas and operated this plant until December 1998. The first production of magnesium from seawater was in Great Britain in March 1940 when Magnesium Elektron used seawater magnesia to produce magnesium chloride. (5)

Germany had been the first into commercial electrolytic magnesium production. They continued research on this and on other magnesium production processes including the use of FeSi to reduce calcined dolomite. There was also extensive experimentation to develop the fabrication technologies, including sand casting, die-casting, forging, extrusion, and rolling. New alloys of magnesium were worked on to improve the properties of the metal. A complete summary of all the knowledge available about magnesium was published in 1939 in a book titled "Technology of Magnesium and its Alloys", by Adolf Beck. It was translated into English by F.A. Hughes in 1940.

The Germans, led by Dr. Gustav Pistor and Mosechel, worked to develop methods of extracting magnesium from carnallite. The chloride was loaded with hydroxyl groups. Mosechel decided in 1924-1925 to chlorinate the oxide at temperatures above the melting point of magnesium chloride. This produced a process to chlorinate calcined and raw magnesite with carbon and chlorine, to produce a truly anhydrous cell feed. To avoid importing magnesite into Germany, a process was developed in 1937 to treat local calcined dolomite with MgCl₂ solutions available as byproducts from the potash industry.

Dr. Pistor and his staff also sought a way of reducing magnesium by a thermal process directly from dolomite. This was forerunner of the process developed by the Italians and by Dr. L. M. Pidgeon in Canada. The Germans used a rocking resistor furnace with internal electrical heating to give a temperature of up to 1400 °C, under vacuum. Furnaces were designed and built that gave a daily output of one ton of magnesium. In 1939, some furnaces of this type were built for the Italian Government and installed at Aosta, where they operated during the war.

In 1929, the British imported almost 60% of the total German magnesium production. This was used for commercial vehicle parts such as bus engines and transmissions.

The British had tried many ideas concerning magnesium production. In 1920, a new group took over the Magnesium Metal Company and its metallurgist E. A. Ashcroft. A plant was built using the Ashcroft process that was based on an electrolytic cell with a molten lead cathode. The magnesium was liberated from fused salt at the cathode producing magnesium-lead alloy. The pure magnesium was recovered from the lead alloy by subsequent salt bath electrolysis. The plant operated until 1923. (5)

In 1935, F. A. Hughes, through their managing director, Major CJP Ball, negotiated an agreement to acquire for the British Commonwealth the patents of I.G. Farben covering Pistor's process for thermal magnesium extraction, and formed Magnesium Elektron Ltd, as the operating company in which I. G. Farben and Imperial Chemical Industries were the other shareholders. In 1936, a works was built at Clifton Junction, Manchester, which was designed to extract 1,500 tons of magnesium metal per year from imported raw and calcined magnesite by the electrolytic process. In 1940, a further unit of 5,000 metric tons per year (mtpy) was built and started production in 1941. In 1942, the Government authorized MEL to erect a further 10,000-mtpy plant at Burnley. (5)

In 1935-1936, Murex Ltd built a 1,000-mtpy magnesium plant at Rainham that used calcium carbide to reduce MgO. In 1940, the Lancashire Metals Subliming Corporation tried to extract magnesium from calcined magnesite and calcined dolomite, under vacuum, using ferrosilicon as the reducing agent. The furnace was a high frequency induction furnace working at 500 kc/s. (5)

In 1938, the Magnesium Metal Corporation was formed in 1938 by the British Aluminium Co. and the Imperial Smelting Corporation to operate the Hansgirg patents for reducing calcined magnesite with carbon. A plant with the potential capacity of 1,000 mtpy of ingot was built at Swansea, Wales in 1939. (5)

The first electrolytic plants in the U.K. used imported raw and calcined magnesite from Greece, Yugoslavia, and India. From 1938, the supply was switched to magnesia obtained from seawater and dolomite. The British Periclase Co. was the first in the U.K. to treat seawater with calcined dolomite to recover both the magnesia from both the seawater and the dolomite. The magnesia obtained was of a highly reactive caustic type, well suited for chlorination to anhydrous magnesium chloride. In March 1939, M.E.L. first used magnesia from the British Periclase Co. and the metallic magnesium extracted was the first recorded commercial production from seawater.(5)

In the U.S., the American Magnesium Corporation (Alcoa) operated the fluoride process until 1927. Dow was the sole primary producer in the U.S. until 1941. Dow used the brines from Michigan to recover bromine, chlorine, sodium, and calcium. In 1940, Dow, advised by Dr. E. O. Barstow, decided to make use of the many natural advantages of Freeport, Texas to cheapen magnesium production costs and use seawater as the source of magnesium. Dow was producing 2,500 tons of magnesium in 1938, which was the total supply for both the U.S. and Canada.(5)

The Norwegian, Christian Backer, who ran the Canadian magnesium production at Shawinigan, went back to Norway and started De Norske Saltverker AS to produce magnesium and extract salts from seawater at Fotlandsvag outside of Bergen, Norway. The plant started operation in 1920 and reached a yearly capacity of 500 tons before it closed in 1922. Backer developed processes for the production of magnesium pistons and piston rods made in a permanent mold in a magnesium-aluminum-cadmium alloy. (6)

In Japan, in 1928, Mr. K. Nagayasu and Dr. R. Matsuura started research into the development of a magnesium production process at Ube in Yamaguchi Prefecture. In 1931, the Institute of Physico-Chemical Research built a magnesium pilot plant at Kashiwazaki, Japan. The first plant to produce the metal in commercial quantities was built at Ube, Japan, in 1933 by the Riken Metal Manufacturing Co. Magnesium production development was continued through the start of World War II. (7)

Magnesium development in Russia was accomplished after a great deal of scientific investigation. These investigations covered the physical-chemical properties of magnesium cell electrolytes; and the design and testing of magnesium electrolytic cells and other equipment. These studies were carried out between 1929 and 1936, under P.P. Fedotyev, P. F. Antipin, Yu. V. Baimakov, V. M. Gus'kov, I. G. Shcherbakov, S. V. Karpachev, and others. Technological processes for the production of magnesium were developed in fairly short time. In 1931, a magnesium pilot plant began operating in Leningrad and was used for the R&D work on the technical methods of production of anhydrous magnesium chloride, electrolysis, and casting and refining of magnesium. Work in this field was also conducted at the All-Union Aluminum and Magnesium Institute, and installations were designed for the first magnesium plants to be erected in the Soviet Union. (8)

After some administrative delays, the technology was transferred to Zaporozhye and to Solikamsk, and magnesium production plants were constructed at these sites. The first production was at Solikamsk in March 1936. The plant operations were improved and the plant reached its design capacity of 1,000 mtpy by the end of 1937. The Zaporozhye plant was a bit slower in starting up as the raw materials for the cell feed were not as pure as those at Solikamsk.

The S. A. pour la Fabrication du Magnesium in Switzerland produced magnesium in small quantities (500 tons per year) at its Martigny-Bourg plant from 1926 to 1947.

WORLD WAR II

The actual period of magnesium during World War II varies depending on what country is mentioned. Traditionally, in the U.S., 1941 is considered as the starting time of the war, but for Europeans and others, the time was much earlier.

Country	Metric tons per year					
Germany	20,000					
England	5,000					
France	2,500					
United States	2,500					
Japan	1,000					
Soviet Union*	2,000					
Switzerland	500					
* Modified from original with						
information from P. Detkov						

Table 1. World production of magnesium in 1938Source: The History of Magnesium, Major CJP Ball

The German industry was quietly developing magnesium production in the 1930's. By 1938, they produced more magnesium than the total of all of the magnesium producers in the world. The military need for magnesium in Germany required the continued expansion of the industry to a peak of 34,000 tons per year (tpy) in Germany itself. The Germans also built new plants at Mossienbaum, Austria, 20,000 tpy and at Heroya, Norway, 10,000 tpy. Another plant of 24,000 tpy capacity was built at Vienna, Austria, but was destroyed by bombing before completion. In 1944, the plants operating in Germany were Aken, 12,000 tons; Stassfurt, 12,000 tons; Bitterfeld, 4,000 tons; Heringen, 6,000 tons. (9)

In Great Britain, magnesium production was expanded by fully utilizing the existing magnesium plants and by expanding on the existing technology. The production reached a peak in 1943 at 32,000 tons divided up between Magnesium Elektron with 10,000 tons at Lowerhouse; 5,000 tons at Clifton Junction; Murex, Ltd, 6,000 at Rainham; 5,000 tons at Moss End; Magnesium Metals, 1,000 tons at Swansea; International Alloys, 5,000 tons at Cardiff.

Australia, in 1941, built a 1,000-tpy magnesium production plant using the Murex process (thermic reduction of magnesite with calcium carbide). The production never reached rated capacity and the plant, operated by BHP, was shutdown in 1944.

In Switzerland, the plant at Maartigny-Bourg produced magnesium in small quantities until 1947.

In Italy, in 1939, the Samis/Aosta Company was formed to operate the I.G. dolomite-ferrosilicon thermal reduction process. It produced 350 tpy until 1945 when it was closed. The Societe Anonima Italiana per il Magnesio e Leghi de Magnesio was founded in 1938 to erect a plant at Bolzano to operate the Amati process for the extraction of magnesium from the oxide. The Amati process used large internally heated retorts with special large briquettes placed on trays and lowered into the retort. Condensed magnesium crowns from this process were reported to weigh over 450 kg. This plant reached an output of over 4,000 tpy at its peak in 1943. (9)

In France, two modern plants improving on the original electrolytic plants were built at Jarrie, Isere and St. Auban in the Basses-alpes. These plants produced 3,000 tpy using the I.G. process during the first part of the war. During occupation, the plant production dropped to 400 tpy. Lab work done on a thermal reduction process in the 1931-1938 period, but no plant was built. This work was the basis for the Magnetherm process installed in 1964. (9)

In Japan, in 1942, there were six plants producing magnesium. Two plants in Korea and one in Taiwan were operated by Japanese companies. The metal produced in these plants was obtained from magnesite and brines by electrolysis and carbothermic production. Seawater was not used and no silicothermic methods were employed. Production of magnesium by the Japanese doubled during World War II and all of it was used as an alloying element in aluminum, for fighter planes (mainly the Zero), in pyrotechnics, and other war materials. By December 1945, 16 plants were operating in Japan, Korea, and Taiwan to supply Japan's war requirements. (9)

The 10,000-tpy German plant built in Norway in 1940 only operated for several years and was destroyed by bombs.

During the war, Russia increased magnesium production at Solikamsk. The plant at Zaporozhye, in the Dnieper Basin, came under danger from attacking forces. Much of the equipment was moved and key members of the plant staff were transferred to Solikamsk to assist in expanding magnesium production. After the close of the war, the 12,000-ton capacity plant at Aken in East Germany and the 20,000-ton capacity plant in the Soviet zone in Austria, were dismantled and taken to Russia. (10)

The largest major expansion of magnesium production came in the U.S. during 1940-1943. In 1940, Dow doubled the size of their Midland, Michigan plant which used brine for the source of magnesium chloride. At the same time, Dow started construction of its Freeport, Texas plant, which would use seawater as a magnesium chloride source. From 1941-1943, 15 magnesium plants were built in the U.S., 13 by the U.S. government. Of these, eight employed electrolytic processes, six used silicothermic processes, and one used the carbothermic process. U.S. production capacity reached 291,000 tpy in 1943.

In Canada, Dr. L. M. Pidgeon of the Canadian Research Council developed the thermal process that became known as the Pidgeon Process. This process used calcined dolomite and 75% FeSi ground, blended and briquetted into pellets that were charged into closed end, externally heated retorts. A 5,000-tpy plant was built at Haley, Ontario and quickly ramped up in production. This plant is still in operation today.

Country	Number	Total capacity					
Country	of plants	(short tons)					
Australia	1	1,000					
Canada	1	6,000					
France	2	15,000					
Germany	4	35,000					
Italy	4	5,000					
Japan	2	10,000					
Korea	2	5,000					
Manchuria	1	5,000					
Norway	1	10,000					
Switzerland	1	5,000					
U.S.S.R	3 (2)*	4,000*					
U.K.	4	32,000					
U.S.	15	293,000					
Total	41	426,000*					
* New information supplied by P. Detkov							
Zaporozhye not operating in 1943.							
Magnesium was produced at Solikamsk and Berizniki.							

Table 2. Magnesium production capacity in 1943

Source: Magnesium & Magnesium compounds, IC 8201, US Bureau of Mines, 1963.

POST WORLD WAR II TO 2001

For over 40 years, new players have come into the magnesium arena, and they always claim their process is better and the production costs will be the lowest in the industry. And time and time again, the plant operation at rated capacity is severely delayed both by construction and operational problems. When the plant is finally operating near the original rated capacity and the metal guality is satisfactory, the optimistic dreamers have become realists. Talks of great low prices have disappeared and the new plants struggle just to exist. Suddenly it is clear to them that the whole process is much more difficult than anyone ever thought, and the new plants are happy to get the standard market prices for their metal.

One of the big problems is process technology. There are very few processes commercially available that have demonstrated sufficient development to be able to produce magnesium metal economically. The electrolytic processes (except for Dow) require a very anhydrous magnesium chloride. This is the basic area where every

project past, present, and future has had big problems that are still not solved in 2001. Herbert Dow said it was easy to remove the magnesium from seawater, it was removing the water from the magnesium that was difficult.

	Company	Location	${f Mg}$ Source	Process	Туре	Initial Capacity	Comment		
1951	Norsk Hydro	Porsgrun	Sea Watr	Electrolytic	I.G. Farben	18,000	X 1		
1959	AL Metallurg.	Selma, Al	Dolomite	Thermal	Pidgeon	7,000	X 2		
1960	Furakawa	Japan	Dolomite	Thermal	Pidgeon	5,000	X 3		
1964	Pechiney	France	Dolomite	Thermal	Magnethrm	9,000	X 4		
1964	Ube Kosan	Japan	Dolomite*	Thermal	Pidgeon	5,000	X 5		
1969	Nat. Lead	Utah	Brine	Electrolytic	ModifIG	40,000	6		
1970	Am Magnes	Texas	Brine	Electrolytic	ModifIG	25,000	X7		
1972	Dow Chem	Texas	Sea H2O	Electrolytic	Dow Cell	25,000	X 8		
1974	BrasMag	Brazil	Dolomite	Thermal	Ravelli	7,500	9		
1975	NoWst Alloy	Addy, Wa	Dolomite	Thermal	Magnethrm	36,000	X 10		
1985	MagCan	Canada	Magnesite	Electrolytic	MPLC	12,500	X 11		
1992	Norsk Hydro	Canada	Magnesite	Electrolytic	Norsk Hyd	45,000	12		
1993	Dead Sea Mg	Israel	Brine	Electrolytic	VAMI/UTI	35,000	13		
1994	Noranda	Canada	Asbestos	Electrolytic	Alcan	63,000	X 14		
1997	AusMagCorp	QuensInd	Magnesite	Electrolytic	Alcan	1,500	15		
Table 1 Major magnesium prejects since 1050									

Table 1. Major magnesium projects since 1950

Comments:

- X. Plant that was built, operated, and closed.
- 1. Plant expanded and process improved. Output in 1998 at 43,000 tpy + 10,000 tpy recycling. Closed primary production in 2001.
- 2. Pidgeon process plant was put out of business by Dow lowering price from 36 to 30 cents.
- 3. Plant became uneconomic: labor, electricity, and process costs became too high.
- 4. Plant at Marginac has been expanded to 20,000 tpy cap but electrical costs were high. Plant closed in 2001.
- 5. Made dolomite from seawater magnesia and limestone. Process became too costly. Moved plant to China in a joint venture deal.
- National Lead sold to Amax who sold to Renco. Plant was modified in 2001 by changing out NH type of cells in one building and installing a MagCorp developed cell, which seems to be doing very well.
 Mag plant cells were not good, bought Russian technology, had environmental problems, fixed much of that, then evaporation ponds flooded, owner assassinated, sold out to MPLC.
- 8. Dow built a Mag-Chlor plant to produce magnesium and strong chlorine, it did not run well and was closed and demolished after about one year.
- 9. Brazil used a modified Ravelli (Amati) process for the design and construction of their thermal plant. 10. Alcoa established a magnesium production plant using Pechiney technology. The plant is located just north of the old WWII magnesium plant that used the same dolomite deposit. Plant efficiency and capacity have been expanded by Alcoa applied research. Use magnesite to "sweeten" the charge. Plant was scheduled for shutdown on September 30, 2001.
- 11. MagCan was designed and built to process magnesite using a carbo-chlorination process developed by MPLC and piloted in England. The plant used the modified Russian electrolytic cells developed by American Mag. Failed due to combination of technical and partner reasons.
- 12. Norsk Hydro built a new plant in Canada to use magnesite. Process was developed in Norway. The plant was late and over budget and the operations took a long time to get running well. The plant was built in North America to access the auto industry and aluminum alloying. Anti-dumping charges virtually barred the shipment of magnesium from this plant to the U.S., causing the plant to run at half capacity for several years and lose money. Plans to expand are on hold.
- 13. Dead Sea Magnesium is a joint venture of Volkswagen and Israel Chemical Company. It was built to use the Dead Sea brine with technology from a VAMI/UTI consortium using the flowline technology.
- 14. Noranda has been working on a process for asbestos for many years. The process was piloted and now the 63,000 commercial plant is starting up. Work on the process development took about ten years before the pilot plant operation. Plant is experiencing start-up difficulties. Main problem is getting high quality MgCl₂ to feed the electrolytic cells. Noranda shut the plant down in April 2003.
- 15. Australian Magnesium (Queensland Metals) has been working on the magnesium process for producing magnesium from magnesite for over 10 years. A 1,500-tpy demonstration plant was operated for two years to prove the process and provide data for the bankable feasibility study. The financing for a 97,000 tpy smelter has been completed and engineering and construction were under way. The commercial plant was

planned to start producing metal in 2004. Ford Motor has signed an off-take agreement for 1/2 of the production for five years with an option to renew for another five. Base price was said to be \$1.30. Ford also put A\$40 million into the project to help build the demonstration plant.

CURRENT TECHNOLOGY IN COMMERCIAL USE

Electrolytic production

Most of the large magnesium production plants in the world today use electrolytic processes, which generally require magnesium chloride as a feed and use electric current to convert this to magnesium metal and chlorine gas. Some of them use a feed source, such as brine or evaporated bitterns, to produce magnesium chloride. If the feed is an anhydrous magnesium chloride feed, then chlorine (produced as a byproduct) can be purified and sold.

In general, it may be said that plants using magnesite for a feed material will not produce chlorine for external sale. This is because HCl is required to dissolve the magnesite, thereby forming hydrated magnesium chloride (MgCl₂•6H₂O), and the chlorine generated has to be used to produce more hydrochloric acid. This is also true for processes that use asbestos tailings or serpentine as the source of magnesium credits.

There is one big hurdle that has prevented magnesium metal from being produced in much larger quantities. Technical innovation is needed to produce an economic and reliable production process. The electrolytic magnesium process is basically divided into two steps: one to make the anhydrous magnesium chloride, and the other to apply large amounts of electric current to dissociate the feed into magnesium and chlorine. (Theoretically, electrolysis produces 1,100-1,400 g of chlorine for each 450 g of magnesium). The production of anhydrous magnesium chloride is a key stage in the process and is still the cause of most technological problems.

Magnesium chloride is peculiar compound that has six waters of hydration attached to the polar Mg-Cl molecule. As a result of intermolecular attractions, the water molecules cannot be removed easily. Simple drying techniques using heat, remove water until the mixture reaches about 72% magnesium chloride (MgCl₂•1.5H₂O). However, further attempt to apply heat causes the remaining mixture to change to magnesium oxychloride, a stable refractory material.

There is no electrolytic process that is commercially available for license that has any type of guarantee that it will economically produce pure magnesium. There are several feed processes and several electrolytic cells that are available for license, with no guarantee for any of them.

At the present time, the Russian/Ukrainian magnesium groups have processes to sell. Most are based on carnallite as a feedstock. However, Russian specialists have developed several process flow sheets for the production of magnesium from a variety of magnesium oxide feedstocks (magnesite, brucite, serpentine) via the carnallite route. This type of technology was used to build the Dead Sea Magnesium plant in Israel.

Alcan has both a feed process and an electrolytic cell. Neither has been proven in commercial magnesium production. The Alcan cell technology has been licensed to Australian Magnesium. Australian Magnesium Corp. will use its own proprietary processes for producing magnesium chloride. U.S. Magnesium LLC (formerly Magnesium Corporation of America, MagCorp) has recently installed 30 new cells that were designed and developed by the MagCorp research group. Dow has recently licensed their feed production and electrolytic cell technology to Magnesium International (formerly Pima Mining NL) that has the SAMAG magnesium project in South Australia.

Thermal processing

There are several major thermal processes that have been used for magnesium production over the past 70year period. Most of the plants have been small and highly labor-intensive. In general, the processes use a reducing agent, such as silicon, to reduce magnesium oxides under a vacuum. The magnesium oxides are derived from many sources. At the present time, both dolomite (MgCO₃•CaCO₃) and magnesite (MgCO₃) are the main sources of magnesium. The most widely used thermal process is the one developed by Dr. Lloyd Pidgeon (11) using horizontal, alloy steel retorts. It has been used in the United States, Canada, India, Japan, and the United Kingdom. In the last ten years, China has developed a very large magnesium production capability based on the Pidgeon process. (12)

The Pidgeon process entails filling a closed end, alloy steel tube with a briquetted mixture of calcined dolomite and ferrosilicon. The tube is heated (usually in a furnace) under a vacuum and the reduction of the magnesium oxide takes place. It is not practical to operate continuously, because the retorts have to be emptied and recharged several times per day.

In contrast, the Pechiney Group in France has developed a large vertical furnace with an electric resistance design that uses ferrosilicon to reduce calcined dolomite in a molten bath containing alumina. The Pechiney Magnetherm furnace can operate continuously for about one day before the accumulated molten slag has to be tapped out from the interior of the furnace and the condensed metal in a large condenser is removed and replaced with an empty condenser.

The Brasmag process in Brazil uses a modified silicothermic process that has a large, internally heated reactor. It produces a large amount of magnesium vapors and a large condensed deposit.

Summary of today's magnesium

Country of	Total Mg produced,	Total thermal	Type of thermal		
production	metric tons	${f Mg}$ produced	process		
United States	40,000	0			
Canada	45,000	7,000	Pidgeon		
Brazil	9,000	9,000	Bolzano (Ravelli)		
PR of China	260,000	260,000	Pidgeon		
France	0	0	Magnetherm		
Serbia	2,000	2,000	Magnetherm		
India	0	0	Pidgeon		
Russia	40,000	0			
Ukraine	2,000	0			
Norway	0	0			
Kazakhstan	10,000	0			
Total	408,000	278,000			

Table 1. 2003 World magnesium production

(table based on Author's personal estimates)

In 2003, total world magnesium production will be approximately 408,000 metric tons (mt) (6). For many years, the leading and largest magnesium producing country was the United States. However, with the recent plant closings and the rapid increase of production in the Far East, China is now the world's largest producing country. Table 1 shows that over 60% of the world's production of primary magnesium is produced by thermal processes.

Dolomite has been used for magnesium production in the United States, Canada, France, China, Serbia, India, and Brazil. Magnesite is used for magnesium production in Australia and in Canada (Norsk Hydro imports magnesite from China and Australia for its Becancour plant), using several new processes. The 63,000-mt Noranda magnesium plant uses asbestos tailings as the source of magnesium.

There is one primary magnesium producer in Europe (Serbia). It uses thermal processing (Magnarohm). Much of the European magnesium requirements come from China and Russia. Salt brines are used for magnesium production in several major regions in Russia and Kazakhstan. In the U.S., Magnesium Corporation of America uses solar evaporation to concentrate magnesium-containing water from the Great Salt Lake in Utah. The Dead Sea Magnesium plant produces magnesium from evaporite deposits of the Dead Sea in Israel. Both major

Russian magnesium producers (Solikamsk and Avisma) use carnallite salts from the evaporites in the Perm region of Russia.

MAGNESIUM IN CHINA

It is necessary to say a few words about China and magnesium. They have accomplished several important steps in ten years by taking a technology (Pidgeon Process) that was considered obsolete and uneconomic by the world magnesium community. Now we have a situation where it is important to recognize:

- 1. The largest magnesium producing country in the world is China.
- 2. The largest magnesium exporter is China.
- 3. China's annual output of primary magnesium in 1999 is estimated to be 25 times as much as that in 1980.
- 4. During the 1994-1999 period, the magnesium production grew at an average annual rate of 40.8%.
- 5. In the nearly thirty years from 1958 to 1987, there was one magnesium plant in China. At the peak of 1995, there were more than 300 magnesium plants across the country.
- 6. The silicothermic (Pidgeon) process has been the most suitable and profitable process for the production of magnesium in China.
- 7. After 1997, the magnesium industry in China began a period of capacity adjustment and steady development, which continues today.

Year	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002
Exports	19	7,388	8,992	15,639	46,940	49,126	78,116	99,937	137k	167k	167k	158k

Table 1. Exports of Chinese magnesium products (metric tons)

The status of the Chinese magnesium industry is very dynamic. There are changes every day. The country is so large and there are so many magnesium plants that it is difficult to make a total industry assessment. One of the foremost groups in the development and introduction of Chinese magnesium to the world is Sinomag. They have provided us with some specifics on the larger part of the Chinese production.

Many of the newly, joint venture plants produce only magnesium alloy from primary magnesium crowns that they purchase by contract or on the open market from Chinese primary magnesium producers.

MAGNESIUM PROCESSES FOR TOMORROW

Electrolytic process development

Norsk Hydro

A review of magnesium research and the electrolytic process finds that there has been little major change over the past 40 years. Of the major magnesium producers, Norsk Hydro, made the greatest strides at developing the magnesium production process. They started production in 1951 using an old I.G. Farben process and plant. Today, Norsk Hydro has two processes: one uses magnesite for feedstock; the other uses seawater and dolomite. The feed preparation technology has been highly advanced and the cell sizes dramatically increased to take a current input of over 400,000 amperes.

Norsk Hydro has traditionally not offered their latest technology for commercial licensing. This could possibly change as the company becomes more progressive and interested in a high rate of return on its investment.

Alcan

Alcan, a non-producer of magnesium, has done more research on electrolytic reduction than most companies have. Alcan ran a magnesium plant at Arvida, Quebec using brucite from Wakefield as the feedstock. When this production plant was closed in 1959, research on the electrolytic magnesium process continued. A process development agreement was signed with Osaka Titanium (now Sumitomo Sittix). The cell was jointly developed using byproduct MgCl₂ from titanium production operations as cell feed. The magnesium chloride is anhydrous,

so moisture in the feed was never a big problem during the cell development activities. This work continues while the cell technology is being licensed for commercial use. (14)

Dow Chemical. Dow modified the original Dow cell using the hydrous feed and larger anodes to increase production and increase efficiency over several years. In 1975, there was a concentrated program to reduce the energy required for magnesium production by 30%. Actually, the total savings in a 10-year period were 38%. The cells at shutdown had a capacity of 200,000 amperes with a current efficiency of close to 90%. This was up from the initial loads on the cell of 60,000 amperes in 1938 with 8.9 kWh per pound of Mg with current efficiencies of 75%-80%. Dow decided to get out of the magnesium business after 82 years and licensed the improved magnesium production technology to Pima's 100% owned subsidiary SAMAG for the South Australian magnesium project. Minor design modifications have been made to permit the project to use high-grade magnesite feedstock rather than seawater, which Dow had used at Freeport, Texas.

Noranda

The Magnola project at Danville, Quebec is the first new electrolytic magnesium plant to be built in many years. After a long, careful development period, the researchers at Noranda developed a unique process to produce anhydrous magnesium chloride for cell feed. They are using one of the latest versions of the Alcan Cell technology for the electrolysis part of the plant. The technical advances can be seen in the electrolytic area where 24 Alcan cells were designed to produce 63,000 metric tons of magnesium metal in a year. The maximum actual production with all cells running in 2002 reached 24,000 mt. (The plant had severe start up problems and as of May 1, 2003 has been totally shut down.)

The Magnola process consists of

- 1. Continuous leaching of asbestos tailings (40% MgO, 38% SiO₂, 5% Fe compounds, and 13% H_2O with some CaO and AI_2O_3).
- 2. Partial neutralization of overflows to avoid silica gel formation. Base metals are removed and magnesium precipitation is avoided by adjusting the pH.
- 3. Slurry is filtered producing an impure brine and a residue containing silica and impurities.
- 4. Impure brine is further purified by sparging with chlorine gas to oxidize any remaining iron to the ferric state and to oxidize the manganese to solid manganese dioxide. Fe, Cr, Cu, Zn, Mn, Al, Ni, and B are removed by pH adjustment. The solution is filtered and the solid returned to the leach section in order to recover the converted magnesium. The remaining traces of Ni and B are removed by ion exchange. (15)

A fluidized bed drier is used to dehydrate the purified concentrated brine, containing about 350 grams per liter of MgCl₂ (27 wt % MgCl₂). The concentrated MgCl₂ solution is sprayed through nozzles over the fluidized bed of prills. The prills are transported to a specially designed "Super Chlorinator" where the prills are melted and sparged with HCI (gas) for a final purification prior to being transferred, molten, to a Alcan Multi Polar Cell. The estimated produce kilogram power to of magnesium is said to be 10 kWh. а

Australian Magnesium Corporation (AMC)

An Australian research effort has improved on the Nalco technology for the production of anhydrous magnesium chloride and has operated a 1,500 mtpy demonstration plant with an Alcan Cell to produce magnesium metal in Queensland. The process development (AM process) came from work done by the Australian Research and Development Project comprised of Queensland Metals and CSIRO, the Australian research group. The process uses magnesite as the feed material. It is dissolved in HCl to form magnesium chloride. Anhydrous magnesium chloride is produced by replacing the waters of hydration (MgCl₂•6H₂O) with ammonia (MgCl₂•6NH₃) and the ammonias driven off by special "calcining". The resulting solid anhydrous magnesium chloride is fed directly to an Alcan multi-polar electrolytic cell. A 96,000-mtpy production plant for Queensland was being designed and constructed. (This project is having severe financial problems and there is little chance that it will ever be constructed.)

Magnesium Alloy Corporation (MAC). The CIS magnesium consortium of VAMI and UTI, in cooperation with Salzgitter Anlagenbau of Germany, have developed a feasibility study for MAC of a magnesium plant in the Republic of Congo. The study is based on the unique reserves of magnesium ore (carnallite) and excellent energy sources. The electrolyte cell would be similar to the ones installed at the Dead Sea Works. The projected production costs are very low.

Dead Sea Magnesium

One of the recent developments that established new technology was the design and construction of the magnesium production plant at the Dead Sea in Israel using Russian/Ukrainian technology. This project used the latest CIS combined technology of feed preparation and flow line technology.

Writer's personal note: After World War II, there was a large and concentrated effort on the development of light metals in many areas of the USSR. The political situations prevented much exchange of information between the west and these scientific efforts. Occasional manuscripts and papers were presented, but in general, much of the Western magnesium community was unaware of the depth of work being done in studies on dehydration of magnesium chloride and cell development.

Most English speaking Western countries are not communicative in the Russian language. The only insight into much of the work that was being done came through a few works that became available in the West. Ermakov, Eidenson, Strahlets, Muzhzhavlev were some of the Soviet authors that were translated into English during the "quiet" period. Much of the research effort was centered at the All-Union Aluminium Magnesium Institute (VAMI). However, the Ukrainian Titanium Institute, the various research centers at the magnesium production plants, and several other major groups also worked during the 50-year period 1950-2000 to develop and improve magnesium production technology.

There was much cell experimentation with bottom anodes, diaphragmless cells, molten metal refining, and alloy production. One of the first Americans to recognize the advantages of the improvements in the USSR was Roger Wheeler, U.S. magnesium pioneer and developer of the American Magnesium Company in Snyder, Texas. In 1971, he removed the modified I.G. type electrolytic cells and installed the diaphragmless electrolyzers at his plant in the small West Texas oil town. Technologists from USSR were used to assist in the modifications. (The headlines in the local Texas papers said, "The Russians are coming, the Russians are coming.") These cells were modified over a period of years and after the closing of American Magnesium were used at the MagCan plant in Calgary, Alberta, Canada.

Over the past several years, there has been a greater exchange of ideas and information between the East and West. The world magnesium community now has a better understanding and appreciation of the full depth of the technical reliability of the CIS & PRC magnesium production advances.

Thermal process development

Magnesium Technologies Ltd (MTL)

The carbothermic process has long been thought to be the ideal method for magnesium production. Many researchers over the years have worked to accomplish direct reduction of calcined magnesite with carbon. Pilot and commercial plants have been built and operated using a carbothermic reduction process. They were never practical or commercially acceptable.

The general approach is to use a mixture of 76% of magnesia and 24 parts of high volatility petroleum coke. The mix was ball milled, pelleted, and charged to a 3-phase reduction furnace that operated at 1950-2050 °C. Magnesium vapor and carbon monoxide are produced. The separation of the two products requires fast cooling to avoid recombination. Hansgirg (20) used shock cooling with a stream of cold hydrogen. This caused the magnesium metal to condense out as a fine powder, often pyrophoric.

The MTL group has developed a patentable process for a cost effective and environmentally friendly carbothermic process for the production of magnesium. The process has been tested in a batch-mode pilot plant. The company is reported to be in the process of constructing a continuous mode pilot plant for further process definition. (21)

CONCLUSIONS AND REFERENCES

Magnesium as a structural material has achieved most of its development in the 20th century. The industry is growing steadily and the metal and its alloys are increasingly in demand.

Much research on magnesium processes is being performed in many areas throughout the world. The exploration into more efficient methods is bordering on a very large breakthrough to a very efficient and lower cost process.

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