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DOE/CS/40284-T1

ENERGY

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AN ASSESSMENT OF MAGNESIUM PRIMARY PRODUCTION TECHNOLOGY

Final Report

By
Merton C. Flemings
George B. Kenney
Donald R. Sadoway
Joel P. Clark
Julian Szekely

February 1, 1981

Work Performed Under Contract No. AC01-76CS40284

Massachusetts Institute of Technology
Materials Processing Center
Cambridge, Massachusetts

U. S. DEPARTMENT OF ENERGY

Division of Industrial Energy Conservation

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Price: Printed Copy A09
Microfiche A01

DOE/CS/40284-T1
Distribution Category UC-95f

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Submitted to:

United States Department of Energy
Office of Industrial Programs
Washington, D.C.

Final Report:
Contract Number EX-76-A-01-2295, Task 4 3
February 1, 1981

Dedicated to

Dr. E. F. Emley

A gentleman, a celebrator of life,
and a dean of magnesium technology.

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1. EXECUTIVE SUMMARY

1.1 SUMMARY CONCLUSIONS

At current production levels, direct energy savings achievable through realistically obtainable process improvements in primary magnesium production are small; they are estimated at 1.2 milliquads of energy per annum. Were magnesium to penetrate the automotive market to an average level of 50 pounds per vehicle, the resultant energy savings at the production stage would be somewhat larger, due to the increased production requirements -- about 3.2 milliquads per annum. However, with this penetration, the resulting savings in gasoline from the lighter weight automobiles would conserve an estimated 325 milliquads of energy per year, or reduce the oil import requirement by 62 million barrels of oil per year.*

The principal barrier to more widespread use of magnesium in the immediate future is its price, specifically its price ratio with respect to aluminum (1.64 to 1 on a weight basis and 1.06 to 1 on a volumetric basis). It appears that a price reduction of magnesium of only about 10 percent (and one which is perceived to be long lasting) would be sufficient for widespread conversion of aluminum die and permanent mold castings to magnesium. Other potential barriers to the use of magnesium, including corrosion and current lack of casting or machining facilities, are small in comparison to this small price difference.

In the long term there are some inherent technical and resource availability factors that heavily favor much more widespread use of magnesium. A major one of these is energy. The energy required to produce a cubic inch of primary aluminum in today's production facilities is 20

---

*Note: The above calculation assumes a 100 million car fleet, with magnesium replacing ferrous materials. If magnesium replaces aluminum, the net energy savings is still large, 110 milliquads.

percent more than to produce an equivalent amount of magnesium. As energy costs continue to escalate, this factor alone must favor a long term decline in the magnesium to aluminum price ratio. In addition, the minute amount of magnesium yet produced in comparison with aluminum means that the processes for producing magnesium are not yet as developed, refined, or efficient as those for aluminum; i.e., there is a greater untapped reservoir of potential process improvement in the case of magnesium -- with concomitant cost reductions. The assured availability of low cost magnesium ore within the territorial United States is still another factor. Finally, the continuing demand for ligher weight automobiles must favor magnesium in the long run. Even at today's price of magnesium and gasoline, much greater usage of magnesium in automobiles is cost effective in terms of total life cycle cost to the consumer and it is clearly in the national interest for this usage to increase.

At present there are two basic groups of processes employed for the production of magnesium. There are the metallothermic processes, in which magnesium oxide is reacted with a reducing agent in an electric furnace under vacuum, and there are the electrolytic processes, where both hydrous and anhydrous magnesium chloride melts are subjected to electrolysis. The principal drawbacks of the thermic operations are the need to operate at greatly reduced pressure together with the fact that a solid rather than a molten product is being obtained, and that condensers are relatively inefficient. The main drawback of the electrolytic systems is the high cost of feed preparation. As noted above and elsewhere, the relatively small scale of magnesium production, both in absolute terms and on a per-plant basis, has been an impediment to major process improvements. There are significant opportunities for upgrading magnesium production technologies through improving existing operations, and through the development of radically innovative technologies.

While there is a clear need for a research and development effort in order to make the more widespread utilization of magnesium economically feasible, there is no natural constituency for initiating such a program. Markedly increased magnesium utilization is, however, clearly in the nation's best interest, and the United States Department of Energy could play a central role in catalyzing and fostering a research and development effort toward this end. Numerous research opportunities are listed in this report. Of priority are: (1) improved methods for preparing anhydrous feeds, (2) improved cell technology, to include inert anodes and cathodes, (3) thermochemistry of metallothermic reactions, and (4) the development of continuous metallothermic operations.

1.2 INTRODUCTION

The purpose of this investigation has been to assess magnesium production technologies both technically and economically as a basis for future government programming in process research and development. This work was motivated by the fact that the use of magnesium as a structural automotive material would result in a significant weight reduction and hence could make an important contribution to the conservation of hydrocarbon based energy sources. However, the price of magnesium has been a major barrier to its more extensive use by the the automobile industry. For this reason an important focal point of the study was to examine current magnesium production technologies with a view to identifying research and development opportunities which could lead to a significant reduction in the cost of magnesium production and hence its greater use in the transportation sector.

While much energy can be saved through improvements in primary processing of magnesium, the major energy savings result from the reduced fuel consumption of vehicles in which it is used. At current production levels, the potential direct energy savings in primary U.S. magnesium production through processing improvements are quite small. These are estimated to be 1.2 milliquads per annum. Were magnesium to penetrate the automotive market to an average level of 50 pounds per vehicle, the resultant energy savings at the production stage would be somewhat larger, due to the increased production requirements -- about 3.2 milliquads per annum. However, with this penetration, the resulting savings in gasoline from the lighter weight automobiles would conserve an estimated 325 milliquads of energy per year, or reduce oil import requirements by 62 million barrels of oil per year.*

The energy efficiency of magnesium in automotive applications is a function of its low density: aluminum is 1.55 times heavier than magnesium and ferrous alloys are 4.52 times heavier. It is this low density, combined with strength and ductility comparable to that of aluminum die casting alloys, which makes magnesium particularly attractive for use in transportation applications where weight reduction and fuel economy are directly related.

The range of competitive automotive materials and the percentage

---

*Note: The above calculation assumes a 100 million car fleet, with magnesium replacing ferrous materials. If magnesium replaces aluminum, the net energy savings is still large, 110 milliquads.

weight reduction potential of each is presented in Table 1.2.1. With a direct weight reduction potential of 75 percent when substituting for cast iron, magnesium is the premier light weight automotive material, even when compared with graphite fiber reinforced plastics which have a 60 to 70 percent direct weight reduction potential.

The critical parameter with respect to light weight materials substitution in automotive applications is net life cycle energy efficiency. Stated simply, this is the difference between the energy conserved in use due to reduced vehicle weight and the energy required to produce the component. By this definition, magnesium is by far the most energy efficient of the light weight materials available for automotive use. Over the 100,000 mile service life of the average automobile, the following net gasoline savings over iron based materials are possible:

Material	Net Life Cycle Energy Savings (gallons)
Magnesium	4.2
Aluminum	2.8
Plastics	2.7

To a first approximation, the use of 2 pounds of magnesium in an automobile conserves 1 net gallon of gasoline per annum, or the use of 50 pounds of magnesium in 100 million automobiles conserves 2.6 billion gallons of gasoline per year.

To this point the discussion has dealt solely with net life cycle energy savings as a result of magnesium substitution in automotive applications. The energy advantage of magnesium is not restricted to transportation. As shown in Table 1.2.2, for any cast form application, on a volumetric basis, 20 percent more total energy is required to produce an aluminum component than the magnesium equivalent. Furthermore, in large scale casting

Table 1.2.1

Candidate Alternative Automotive Materials

	Percent Direct Weight Reduction Potential
<u>Wrought Material</u>	
Low Carbon Steel (LCS)	--
Dent Resistant Steels	10 to 20
High Strength/Low Alloy Steel	15 to 30
Ultra-High Strength Steel	40 to 50
Aluminum (Al)	50 to 60
<u>Metal Castings</u>	
Grey Iron	--
Al Die Casting	50 to 60
Al Permanent Mold Castings	50 to 60
Zinc Die Casting	10 to 40
Magnesium Die Casting	75
<u>Plastics</u> (Relative to LCS)	
Unidirectional Fiberglass Reinforced Polyester or Epoxy Resin	50
Sheet Molding Compound Random Fiberglass-Reinforced-Polyester Resin	35 to 50
Unidirectional Graphite Fiber Reinforced Epoxy Resin (Hybrid Reinforcement with Fiberglass, Where Possible)	60 to 70
Continuous Fiberglass Reinforced Nylon "STX" Hot Stampable Sheet	35

Adapted from: Proceedings of Conference on Basic Research Direction for Advanced Automotive Technology, U.S. Department of Transportation, Boston, April, 1979.

TABLE 1.2.2

Comparison of Energy Requirements to Produce Magnesium and Aluminum Castings on Volumetric Basis

	MAGNESIUM	ALUMINUM	% DIFFERENTIAL
Energy required to produce primary metal (BTU/in^3)	9,084	10,752	18%
Energy required to form the casting (BTU/in^3)	566	828	46%
Total energy requirement (BTU/in^3)	9,650	11,580	20%

operations today, magnesium is fully cost competitive with aluminum. An example of this is the choice of magnesium or aluminum in Omni/Horizon transaxle housings as a function of monthly price fluctuations in these two metals.

The comparisons of the preceding paragraph are based on the magnesium and aluminum production technologies as they exist today, where magnesium tonnage is but 3 percent that of aluminum. Because of this, far less research effort has been spent on magnesium than on aluminum. There remains, in the case of magnesium, a very large untapped potential of process and product developments and improvements through research and development.

As for the long term availability of raw materials, magnesium is present domestically in essentially inexhaustible amounts in seawater and brines. There are additional domestic resources, principally in the form of magnesite and dolomite. In contrast, 90 percent of the bauxite and alumina required for the production of aluminum must be imported. While there are alternative domestic mineral resources for aluminum, these require even more energy than bauxite in their processing.

It is an important and clear conclusion from this work that over the long range (e.g., 20 years) magnesium will capture a very large share of the die and permanent mold casting market now held by aluminum. The reasons for this are simple and summarized above. They include (1) the near current price competitiveness of magnesium with aluminum on a volumetric basis, (2) the fact that the energy requirement to produce aluminum components is 20 percent higher than magnesium on a volumetric basis, (3) the ready availability of low cost domestic magnesium resources, and (4) the life cycle energy savings for applications in the transportation sector.

1.3 THE ECONOMICS OF MAGNESIUM

Historically, the limited availability of magnesium and the dominant position of a single producer in the United States have restricted its use in transportation applications. This is partially due to the long-standing policy of the domestic auto industry of requiring at least dual sources of supply to ensure availability. Following World War II, only Dow Chemical Company remained as a major supplier of magnesium. It was not until the early 1970's that several other large scale producers entered the magnesium industry. However, these producers have experienced start-up and operating problems which have caused extensive interruptions of production. Consequently, magnesium continues to be used sparingly -- less than 1 pound per average domestic automobile. With few other structural applications, magnesium production has lagged far behind that of other light weight materials such as aluminum, Figure 1.3.1.

Magnesium has been used in automobiles for nearly fifty years. It has been most successful in Europe where as much as 45 pounds were used in the Volkswagen Beetle. The success of this very popular vehicle has amply demonstrated the technical feasibility of die cast magnesium as an automotive material. Many of the past and current automotive applications of magnesium are listed in Table 1.3.1.

In automotive applications, magnesium is most competitive in cast form, where it competes primarily with aluminum. The threshold point for magnesium to be competitive with aluminum occurs when the magnesium to aluminum price ratio is about 1.7. However, significant usage of magnesium in the automotive industry will probably require a stable long-term price

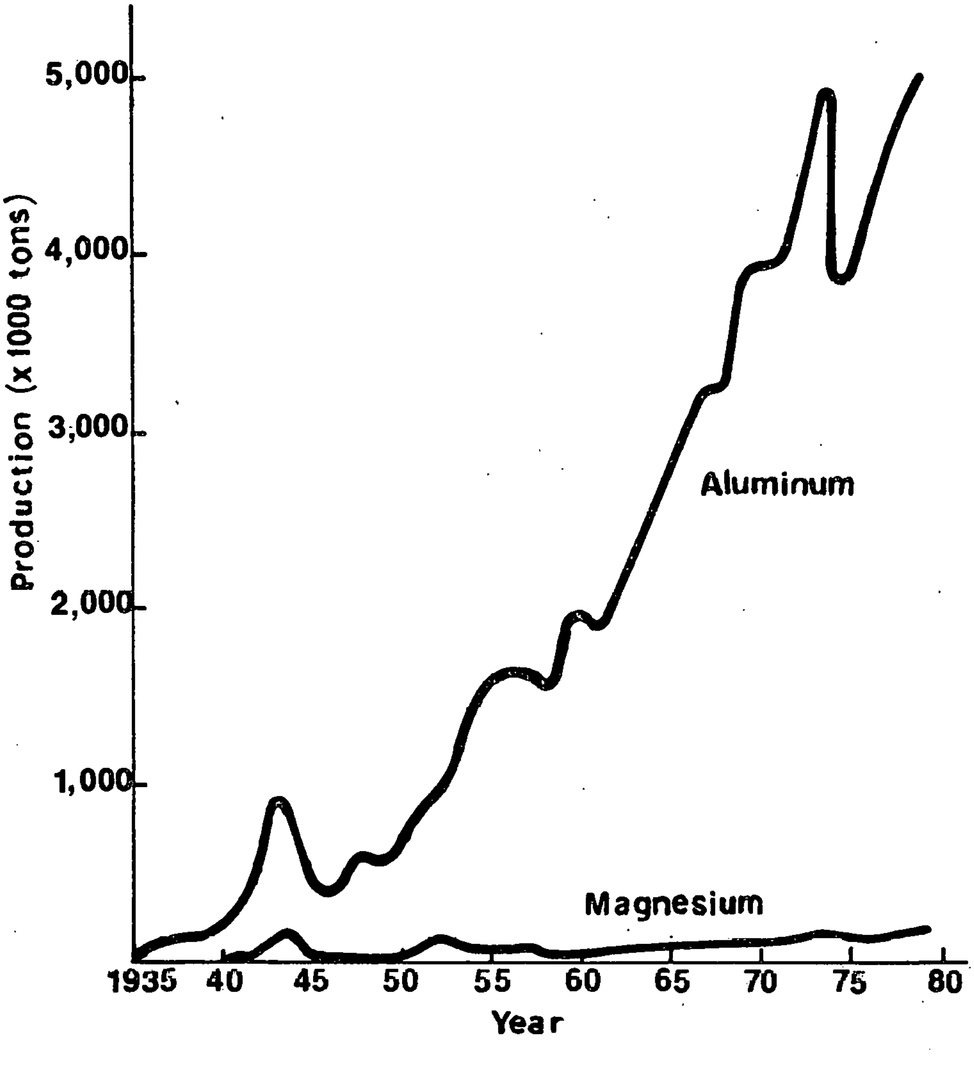


Figure 1.3.1: U.S. Production of Magnesium and Aluminum (X1000 tons).

Table 1.3.1

Past and Current Automotive Applications of Magnesium

U.S.

Power Train

Oil reservoir cover
Generator end plates
Starting motor end plates
Main bearing oil seal
Fan spacer
Fuel pump combination body
Fuel pump body
Fuel pump diaphragm support
Fuel pump air body
Fuel pump pulsator cover
Fuel pump cover
Glove compartment door
Oil filter body
Oil filter bypass valve body
Super charger impellor
EGR valve
Engine front oil seat plate
Blower impellor
Ignition distributor housing
Oil pump and cover
Distributor vacuum diaphragm housing
Torque converter housing (10,000 only)
Clutch housing (3,000 only)
Transmission stator blade
Transmission shift rail guide
Transmission housing (imported)

Body and Chassis

Instrument panels
Instrument panel bezel
Steering column bracket
Steering column clamp
Steering column shroud
Instrument panel filler
Shift lever shaft guide
Gear shift lever bracket
Gear shift bowl and assembly
Horn button bezel
Window actuation mechanisms
Internal window bracket
Turn signal switch housing, cover and plate
Convertible top fold mechanism
Convertible top headers
Heater blower assembly
Defroster grill
Switch mounting plate, steering column
Instrument panel shroud
Steering column lock housing
Sail mirror cover plate

Europe

Power Train

Crankcase, aircooled
Clutch housing
Transmission housing
Transmission housing cover
Transaxle housing
Automatic transmission transfer plate
Oil pump housing
Oil pump trumpet
Valve covers
Engine fan
Covers
Brackets
Pulleys
Transmission support brackets
Dynamo bracket
Transmission bearing support
Steering gear cover
Engine blower housing
Engine blower impellor
Timing gear
Cylinder head cover
Distributor support
Oil filter support
Oil fume engine breather body
Timing chain housings
Suction tubes
Covers for camshaft housings
Gearboxes and covers
Regulator spindle bearing
Camshaft bearing
Regulator box cover
Belt pulleys
Bearing bushing
Wire sheave housings
Bearing bracket
Adapter flange

Body and Chassis

Wheels
Loud speaker frame
Instrument panel
Headlight support
Steering column support
Steering column housing
Tool box and cover

ratio of 1.5 or less (at this ratio the two metals are of equal price on a volumetric basis). The potential automotive usage of magnesium as a function of the magnesium to aluminum price ratio is presented in Figure 1.3.2. This situation, however, is changing and future competition will also include light weight steels, plastics, and composites. Nonetheless, for illustrative purposes magnesium is compared in this analysis with its primary competitor -- aluminum. Given the millions of cars produced annually, it is clear from Figure 1.3.2 that the immediate market potential for magnesium in automobiles is large, if it can be made available at a competitive price.

Currently, automotive usage of magnesium is constrained by its price. During the mid 1970's the price of magnesium rose to more than double that of aluminum, a peak from which it has steadily declined. The price ratio currently stands at 1.64, a level which has been maintained for more than a year. At this price ratio, magnesium is believed to be restricted from large scale penetration of the automotive market as illustrated by the total demand function for magnesium presented in Figure 1.3.3.*

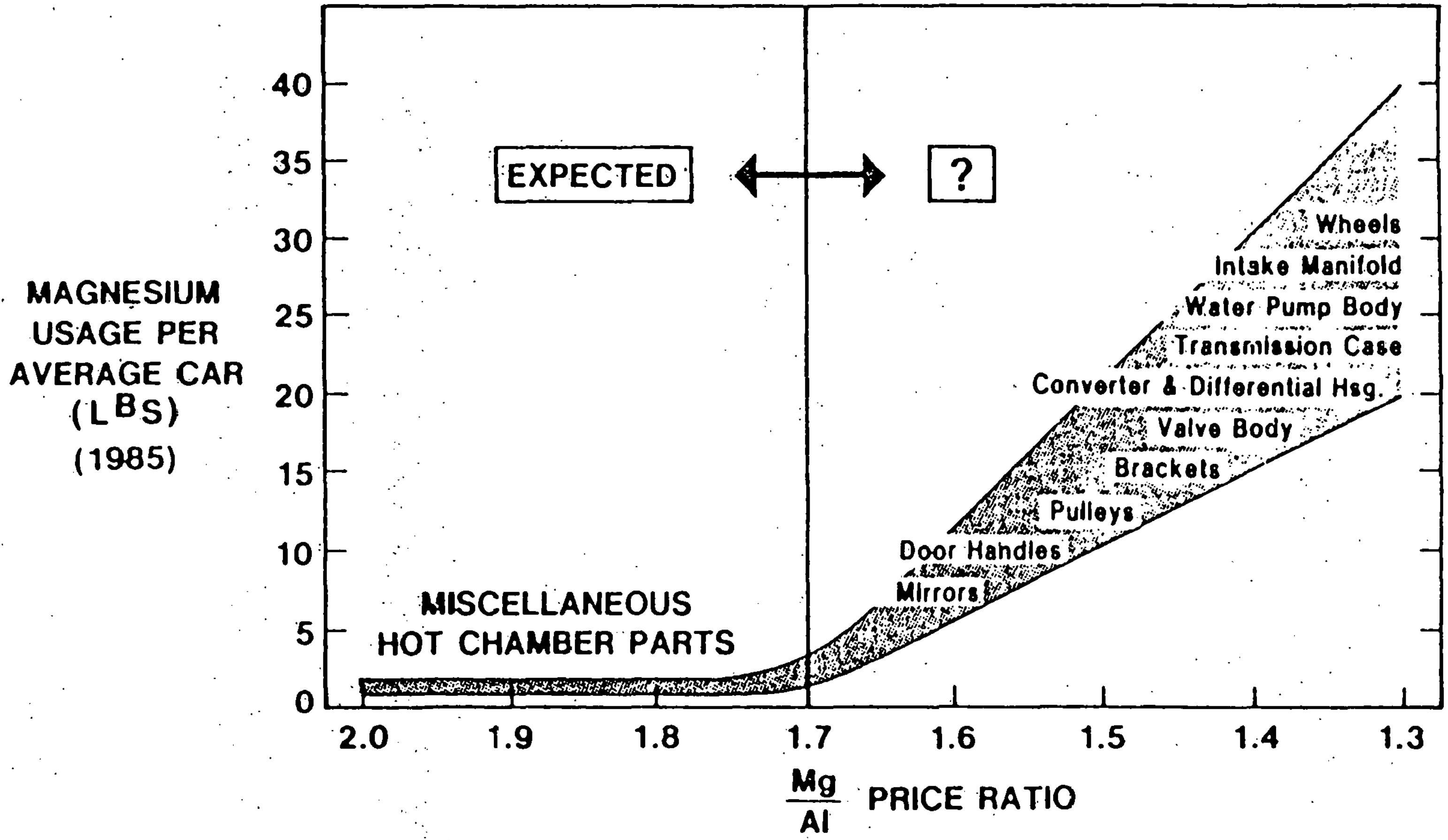
Specifically, at $1.25 per pound, which is equivalent to 1.64 times the price of aluminum, magnesium is priced out of the current elastic automotive market for light weight materials. If magnesium were to decline in price by only 10 percent and maintain that price relative to aluminum, it appears that an automotive market for magnesium approaching the size of the current domestic market for magnesium could be quickly created.

---

*This is clearly true in the present market, even though at the current price level, the life cycle savings from using magnesium in place of aluminum are very large indeed, as discussed in Section 5.1.

Figure 1.3.2:

POSSIBLE MAGNESIUM USAGE BY 1985 AS A FUNCTION OF Mg:Al PRICE RATIO



Source: M. Holland, Ford Motor Company.

Potential large scale industry entrants have been reluctant to invest in magnesium capacity which is solely dependent upon the automotive industry for a market. This hesitancy has been due in part to the presence of a dominant producer and to the uncertain nature of the automotive market for magnesium. The current producers of magnesium share this hesitancy for another reason: an expanded automotive market for magnesium would expose the total market for magnesium, which currently enjoys price stability, to the price instability of the competitive market for light weight materials.

Given the current structure and capacity of the United States magnesium industry, the price for magnesium relative to aluminum cannot be expected to decline soon, and so the automotive market for magnesium cannot be expected to expand rapidly -- unless some external factor is added to the equation such as a technologically aggressive new competitor with adequate capital, or extensive federal encouragement of research and development and investment in magnesium.

Substantial improvements in the production efficiency of magnesium technologies do appear to be possible through process innovations. Such improvements could allow for significant reductions in the price of magnesium, and if these price reductions were passed on to users, magnesium could become fully competitive with other light weight materials by the end of the decade. Process improvements and innovations required to achieve high efficiency magnesium production are recommended in Chapters 3 and 4.

In the opinion of the writers, the current and potential costs of producing magnesium by the electrolytic versus the metallothermic route are sufficiently close that the optimum magnesium primary production processes depends, not on an intrinsic technological advantage, but rather site selection with respect to the availability of raw materials, energy, labor, and markets for both magnesium and process by-products. Given the variation in resources of industrial regions within the United States, electrolytic and metallothermic magnesium production technologies can both be expected to remain competitive for at least the medium term (20 years). Carbothermic technologies have long range potential advantages but no clearly competitive process has yet emerged.

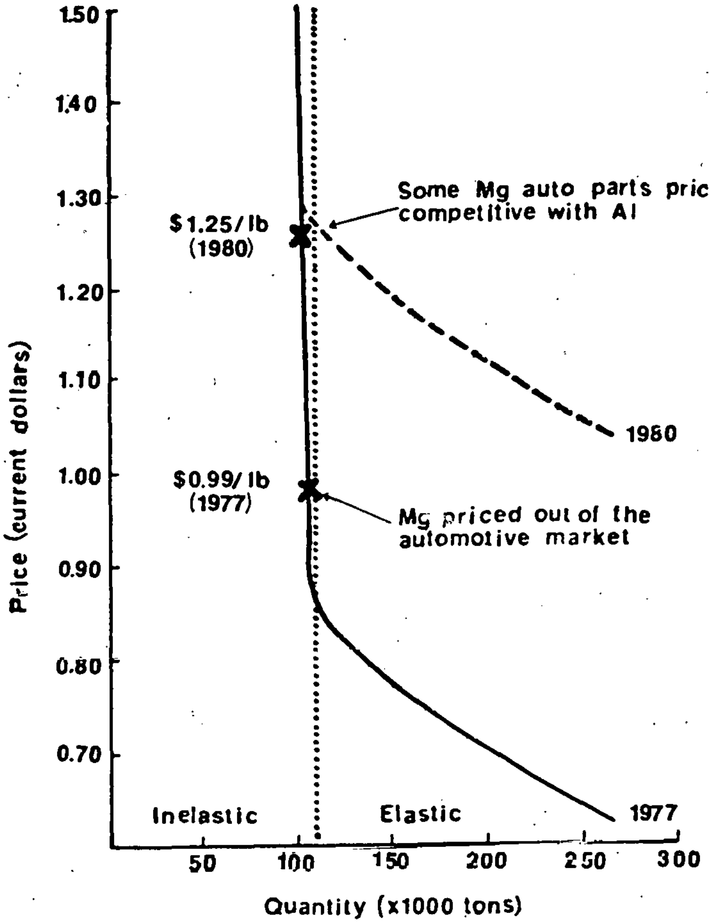


Figure 1.3.3: Total Magnesium Demand Function.

1.4 TECHNOLOGY

1.4.1 General Observations

Magnesium is an abundant component of the earth's crust, 2.35%, but the high stability of its oxide prevents its easy extraction. While there are several technically feasible ways of producing magnesium, the two technologies that deserve prime consideration are electrolytic and metallothermic. Both can be substantially improved with respect to production rate and energy consumption by the application of recent advances in processing science and/or by the development of radically new technologies.

The carbothermic process must also be considered in the long term because of its direct use of energy and subsequent potential energy efficiency. However, this technology is not currently being used, and an extended research and development effort would be required to bring it on-stream as a cost effective process.

1.4.2 Electrolytic Processes

In the electrolytic production of magnesium, molten magnesium chloride is electrolysed to produce molten magnesium metal and chlorine gas. Electrolysis currently accounts for about 72 percent of the approximately 300,000 tons of annual magnesium production capacity in the Western World. The process involves two major steps: (a) feed preparation for the electrolytic cell, (b) electrolysis itself.

The starting material of current electrolytic magnesium processes is some form of an aqueous solution of magnesium chloride: seawater, brine, or certain industrial wastewaters. Before electrolysis, this material must be purified of other salts and dehydrated. The dehydration is nontrivial because the water is chemically bound; simple heating to temperatures above water's normal boiling point can result in the formation of undesirable oxychloride compounds. There are two approaches to this problem. One is to consume large quantities of energy in cell feed preparation in order to be able to electrolyse at high current efficiencies and to keep cell maintenance costs low. Examples of this anhydrous electrolytic design in which 50 percent of the cost of production is in cell feed preparation are the I. G. Farben, Norsk Hydro, Alcan, and various diaphragmless Soviet cells. The other approach, used exclusively by Dow, avoids the costly final dehydration steps and electrolyses the partially hydrated compound $MgCl_2 \cdot 1.7H_2O$. However, anode consumptiom rates and all maintenance requirements are much higher in Dow cells than in anhydrous cells. Some cell characteristics are given in Table 1.4.2.1.

The attractiveness of electrolytic production is its efficient use of energy in the electrolysis stage. The major drawbacks are the high cost of cell feed preparation and the low metal production rate (pounds Mg produced/unit time/square foot plant floor space).

1.4.3 Metallothermic Processes

In the metallothermic processes, magnesium oxide is reacted with ferrosilicon at a reduced pressure in a resistively heated furnace. The magnesium vapor product is condensed in an adjoining vessel and collected in solid form. The principal inefficiencies are operation at reduced

TABLE 1.4.2.1

Operating Characteristics of Magnesium Electrolysis Cells

	Current (KA)	Voltage (V)	Current Efficiency (%)	Specific Energy (kWh/kg)
Dow	90	6.0	75-80	18.5
I.G.	18-150	5.0-7.0	80-85	15-18
Alcan	80	5.7-6.0	90-93	14
Soviet diaphragmless	200	5.0-6.0	85-90	13-15
Norsk Hydro	250-235		92-93	12-13

pressure and in a batch mode. The forner causes the leakage of air into the furnace which results in the loss of magnesium vapor as magnesium oxide and nitride are formed. Current magnesium vapor losses are roughly 20 percent. The batch operation cycle necessitated by the vacuum operation requires roughly 2.5 hours of down time per 20 hours production cycle.

The preparation of ferrosilicon reductant consumes 42 percent of the total energy requirement of the metallothermic process. By adapting the process to use a low grade aluminum alloy available in municipal refuse, the energy requirements of the reductant preparation stage could be reduced by an estimated 75 percent. In the magnesium reaction vessel itself, modifications to permit operation at atmospheric pressure would improve production and energy efficiency in the reduction stage by approximately 25 percent. Conversion to continuous operation would increase unit production by 14 percent. The combination of continuous operation at atmospheric pressure could increase unit production in the reaction vessel by as much as 43 percent.

1.4.4 Comparison of the Alternative Processes

Table 1.4.4.1 presents a comparison of some characteristics of the electrolytic and metallothermic processes. In practice, both technologies claim to be economical at approximately 10,000 annual tons capacity. T ere is a difference, however, in capacity planning. To expand the capacity of a metallothermic facility, corresponding units of ferrosilicon and magnesium reduction furnaces are required. The

TABLE 1.4.4.1

Comparison of Electrolytic and Metallothermic Process for Magnesium Production

	Electrolytic	Metallothermic
Current world capacity (tons)	218,500	83,000
Maximum plant size (tons)	125,000	26,000
Average plant size	54,625	10,375
Energy requirements (kwh thermal/lb Mg)*	42.8	41.1
Electrical energy requirements	48%	70%
Estimated capital cost for new plant ($/annual ton capacity) Sample plant size: 20,000 annual tons	4,500	3,500

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*To avoid any possible confusion, all energy is given in kWh-thermal. This ignores the potential use of hydroelectric energy (1 kWhE = 3.077 kWhT).

capacity of electrolytic magnesium facilities is increased by adding units of electrolysis cells and expanding the existing electrolyte preparation facilities since a single unit "front end" is more cost effective. Otherwise, both appear to be comparable. Site selection, primarily on the basis of raw materials and electricity availability, is the dominant factor in a choice between these two processes, rather than any intrinsic technological advantage. However, of the technologies available today, electrolytic processing is favored by many for very large installations.

1.5 RECOMMENDATIONS FOR RESEARCH AND DEVELOPMENT

Magnesium is an infant compared to aluminum. With currently less than 20 tons per year of magnesium used in structural applications, this is less than 0.0004% of the domestic production of aluminum. By comparison with the aluminum industry, there simply have not been adequate funds available for production improvements and long range research and development in magnesium.

It is clear that a very large potential exists for a practical payoff from research and development in magnesium primary production technology. A significant part of this report is devoted to recommendations in this matter.

Regarding priorities, at this stage it can be said that the most important problems facing electrolytic processing are dehydration and cell throughput. Metallothermic processing is hindered by the need for costly ferrosilicon reductant and batch operation at reduced pressure.

In the recommendations which follow special attention should be given to those which address these issues.

Electrolytic

From an economic standpoint there is no fully satisfactory commercial dehydration process at present. Its development is essential to the viability of electrolytic magnesium production. Fully half the cost of production is in feed preparation. Additionally, regardless of improvements in cell design, the full advantages of electrolysis are never realized as long as impurities are present in the electrolyte.

The following group of recommendations is directed at cell feed preparation.

RECOMMENDATION D1: *Make the necessary thermodynamic and kinetic measurements of the dehydration of hydrated* $MgCl_2$ *to provide a thoroughly adequate data base for the development of dehydration technologies. Of the current commercial inventions, solar evaporation consumes the least energy. A special effort should be made in studying the product of solar ponding. Optimistically, the latter could be eventually treated in one chemical reaction step to produce anhydrous electrolyte.*

RECOMMENDATION D2: *Investigate the effects of alkali-metal and alkaline-earth chlorides on the dehydration of hydrated* $MgCl_2$.

RECOMMENDATION D3: *Make the necessary thermodynamic and kinetic measurements of the dehydration of hydrated* $LiCl$.

RECOMMENDATION D4: *Investigate the purification of* $LiCl$ *by partial crystallization by measuring the compositions of the crystals which freeze out of typical lithium chloride based electrolyte melts which have been contaminated in a controlled manner.*

RECOMMENDATION D5: *Test the dehydration of* $MgCl_2$ *hydrate both in spray driers and flash calciners to determine lowest contamination levels of* MgO *and* $MgOHCl$.

RECOMMENDATION D6: *Determine mass transfer rates from the carbochlorination of* MgO *in a molten chloride by (i) bubbling chlorine/*HCl *in the presence of finely divided carbon, (ii) bubbling a gas mixture of* CO, HCl *and* Cl_2, *(iii) bubbling phosgene (*$COCl_2$*).*

RECOMMENDATION D7: *Determine mass transfer rates when solid particles of dehydrated $MgCl_2$ containing oxide and oxychloride impurities are chlorinated in a fluidizing bed with (i) chlorine/HCl in the presence of finely divided carbon, (ii) a gas mixture of CO, HCl and Cl_2, (iii) phosgene and determine the parameters which affect the purity of the product so produced.*

RECOMMENDATION D8: *Determine purity levels which can be achieved by elimination of oxygen bearing insolubles in anhydrous $MgCl_2$ by filtration and sedimentation techniques.*

RECOMMENDATION D9: *Verify the claims of purity of disclosed solvent extraction processes and test their commercial viability by analysis of optimum operating parameters.*

The most important problem to be solved in electrochemical cell design is mass transport enhancement. If electrolysis is to compete with large scale pyrometallurgical processes, cell throughputs must be increased. Otherwise, capital costs will become prohibitive.

The following group of recommendations is directed at improved electrolytic cell designs.

RECOMMENDATION E1: *Assess various cell designs by measuring fluid flow patterns of water model representations using cinephotography, hot-wire anemometry, and laser Doppler anemometry. This would be coupled with mathematical modelling of the system along hydrodynamic lines.*

RECOMMENDATION E2: *Measure and compare the operating characteristics of intermediate size molten salt cells with those of laboratory cells and water models.*

RECOMMENDATION E3: *Study the electrode kinetics of magnesium reduction in various solvent melts to determine the parameters which may be adjusted to maximize reaction rates with a view to improving ultimate space/time yields. The techniques to be used include emf measurements, linear sweep voltammetry, chronopotentiometry, chronamperometry, and pulse polarography.*

RECOMMENDATION E4: *Compare the cell performance of vertical monopolar electrodes, vertical and horizontal bipolar electrodes, and porous electrodes.*

RECOMMENDATION E5: *Study the electrode kinetics of chloride oxidation at the anode and subsequent formation of chlorine gas bubbles. Factors affecting anodic overvoltage should be determined as a function of electrode shape, composition, temperature and current density.*

RECOMMENDATION E6: *Search for new materials which can serve as dimensionally stable anodes.*

RECOMMENDATION E7: *Investigate the effects of periodic reversal of electrode polarity and superposition of an a.c. voltage on the d.c. decomposition voltage. A molten salt test cell using several candidate electrode designs would be employed. Obviously one expects no variation in morphology; however, there may be some enhancement in mass transfer rates at the electrode surface caused by the disruption of the melt boundary layer.*

RECOMMENDATION E8: *Test the effects of forced circulation of the electrolyte and ultrasonic agitation of the electrodes. This would be performed on several prototype electrode designs in a laboratory cell.*

Metallothermic

Metallothermic process development is currently constrained by a lack of adequate thermodynamic and kinetic data concerning the thermochemical reduction of magnesium oxides by various reductants. These data are essential to the selection of the optimum reductant-feed material mix and operating conditions. Production of the current ferrosilicon reductant requires nearly 42 percent of the total energy required to produce magnesium and represents roughly a third of total production cost.

The following recommendations are directed at the optimum selection of reductant, feed materials, and operating conditions.

RECOMMENDATION A1: *Make the necessary thermodynamic and kinetic measurements of the pyrometallurgical reduction reactions for the various reductant-raw material combinations over the temperature range of interest, up to 2800°C, to provide a data base of reaction rates, magnesium equilibrium vapor pressures, and activity coefficients for all reductant, raw material, and slag combinations.*

RECOMMENDATION A2: *Determine and evaluate the kinetic relationship between operating temperature, reaction rate, and subsequent energy and operating efficiency for the various thermochemical reductant-feed material combinations.*

RECOMMENDATION A3: *Investigate the availability and determine the purity of low-grade aluminum alloys available from municipal refuse incineration plants for use as an alternative metallothermic reductant.*

RECOMMENDATION A4: *Investigate the current level of development of carbothermic processes for aluminum-silicon production. Determine the feasibility of modifying this process to produce a lower grade, inexpensive aluminum-silicon alloy adequate for use in magnesium metallothermic processes.*

RECOMMENDATION A5: *Identify and evaluate the effects of the impurities found in aluminum-silicon and low-grade aluminum alloys on the production efficiency of the metallothermic reduction process. Ideally, the reation slag would accommodate these impurities. If this is impractical, techniques for removing the specific undesirable impurities should be considered.*

RECOMMENDATION A6: *Investigate the technical feasibility of co-production of magnesium and useful metallic masteralloys with metallothermic technology. Determine the economic impact of the alloy by-product, that is, its effect on operating and capital cost, and overall energy efficiency.*

The most important problem confronting metallothermic technology is conversion from reduced pressure batch to continuous operation at or above atmospheric pressure. Roughly 20 percent of the magnesium vapor currently produced is lost due to air leakage. The removal of the reduced pressure operating requirement would both eliminate magnesium losses within the furnace and facilitate continuous operation. Conversion to continuous operation at atmospheric pressure will require the development of improved condenser and slag removal systems.

The following recommendations are directed at the development of a continuous metallothermic reduction process.

RECOMMENDATION B1: *Support the development of innovative efficient condenser concepts designed to operate at pressures approaching or exceeding one atmosphere. Possibilities include the use of inert carrier gas systems and liquid metal splash condensers.*

RECOMMENDATION B2: *Investigate the potential for modifying current furnace design to accommodate continuous slag removal using a barometric leg, gas-life pump/siphon arrangement, or various other continuous of semi-continuous slag removal techniques.*

RECOMMENDATION B3: *Develop mathematical and experimental models to establish the fluid flow, vapor transport and heat transfer characteristics of the basic metallothermic system.*

RECOMMENDATION B4: *Assess various continuous reactor designs based on the mathematical models of fluid flow and heat transfer phenomena. Construct laboratory scale experimental furnaces to verify the mathematical models.*

RECOMMENDATION B5: *Analyze the operating characteristics of laboratory and intermediate experimental metallothermic facilities to establish the scaling conditions and modify the mathematical models accordingly.*

Carbothermic

The carbothermic process has not been used commercially since the second World War because of production inefficiencies and hazards. However, this process has the potential for being the most energy efficiency of the production processes for magnesium. Some long range research, therefore, should be conducted on this process with the goal of ultimately bringing on stream a reliable, efficient, safe process.

RECOMMENDATION C1: *Develop mathematical and experimental models to characterize the thermochemistry, vapor transport, and heat transfer phenomena of the basic carbothermic process.*

RECOMMENDATION C2: *Initiate a program to evaluate alternative innovative techniques designed to overcome limitations of the current carbothermic process, for example, with respect to magnesium vapor condensation and collection.*

RECOMMENDATION C3: *Explore the further development of the liquid metal solvent process for the production of magnesium beyond the laboratory scale. The critical factors concerning solvent flow through the reactor, solvent recovery, and overall energy efficiency and cost effectiveness must be further studied and evaluated.*

2. INTRODUCTION

2.1 BACKGROUND

The Magnesium Project at Massachusetts Institute of Technology was initiated in 1976 with a systems study of magnesium production and utilization by Kenney, Clark, and Flemings. In conjunction with this research program, an international conference on "Energy Conservation in the Production and Utilization of Magnesium" was convened at MIT in May of 1977. This conference, which was co-sponsored by the MIT Department of Materials Science and Engineering, U.S. Energy Research and Development Administration, and International Magnesium Association, brought together individuals from universities, governments, and industries of many countries. Information and data made available during this conference contributed greatly to the ongoing systems study. At the same time valuable and enduring lines of communication between all parties were established.

The present technical and economic assessment of magnesium primary production technologies was initiated late in 1978 with the sponsorship of the Office of Industrial Programs of the U.S. Department of Energy. The study was conducted by Prof. Merton C. Flemings, principal investigator, Professors Julian Szekely and Joel P. Clark, co-principal investigators, and Dr. George B. Kenney, Prof. Donald R. Sadoway, and Prof. Floyd R. Tuler.

2.2 METHODOLOGY

The critical examination of magnesium production technology was a major task which required not only information freely available in the open literature, but also information usually regarded as confidential by industrial organizations.

For this reason an extensive literature survey was complemented by numerous personal discussions with industrial representatives and consultants at Massachusetts Institute of Technology, at conferences, and on site. Visits were also made to plants and laboratories to view ongoing production, research, and development work. Many current and potential producers and consumers of magnesium have contributed greatly to our effort. Much of the data and information made available to this research group, both confidential and unrestricted, could not have been collected without these individuals and organizations. This cooperation and the candor with which materials were made available are greatly appreciated. A partial listing of contacted individuals and organizations is given in Table 2.2.1.

This extensive data base, in conjunction with further thermodynamic, electrochemical, and economic calculations gave new insights into the technological and economic issues at hand. The report is organized as follows:

- Chapter 1 is the Executive Summary
- Chapter 2 gives the background of the project, outlines the methodology, and lists publications and presentations
- Chapter 3 assesses electrolytic magnesium production technologies and makes recommendations for research and development
- Chapter 4 assesses thermic magnesium production technologies and makes recommendations for research and development
- Chapter 5 discusses the economics of expanded magnesium production and utilization

TABLE 2.2.1

Organizations Contacted During This Study

Aluminum Company of America

Aluminum Company of Canada

Alusuisse

American Magnesium Company

Avery Magnesium

Bayliss Industries, Inc.

Billiton Research B.V.

Bureau of Mines, Salt Lake City Metallurgical Research Center

Centro Technico Aeroespacial, Brazil

Dow Chemical Company

International Magnesium Association

James Macey

Magnalith Corporation

Nalco Chemical Company

NL Industries/Doehler Jarvis Castings

Norsk Hydro

Stanford University

SOFREM

University of Illinois

Note: Informal discussions were held with many other current and potential producers and consumers of magnesium.

2.3 PUBLICATIONS AND PRESENTATIONS

As part of this project contributions have been made to the technical literature. These publications, reports, and presentations are listed below.

Publications

(1) Report from the International Conference on Energy Conservation in the Production and Utilization of Magnesium, edited by Merton C. Flemings, et al., Conference held at MIT, Cambridge, MA, May 1977.

(2) G. B. Kenney and J. P. Clark, "Magnesium: Energy Panacea?", American Metals Market - Minor Metals Section, August 18, 1977.

(3) G. B. Kenney and J. P. Clark, "An Analysis of Pricing in the Domestic Magnesium Industry," Proceedings of the Council of Economics of the IME, March, 1978.

(4) G. B. Kenney, An Analysis of the Energy Efficiency and Economic Viability of Expanded Magnesium Utilization, Garland Publishing Series of "Outstanding Dissertations Bearing on Energy," 1979.

(5) M. C. Flemings and G. B. Kenney, "Materials Research for the Fuel Efficient Automobile," Report to the Transportation Systems Center, U.S. Department of Transportation, October, 1979.

(6) M. C. Flemings and G. B. Kenney, "Materials Substitution and Development for the Light Weight, Energy Efficient Automobile," Report to the Office of Technology Assessment, Congress of the United States, February, 1980.

(7) G. B. Kenney, D. R. Sadoway and M. C. Flemings, "An Assessment of the Potential for Magnesium Penetration of the U.S. Automotive Industry," Proceedings of the 37th International Magnesium Association

(8) J. P. Clark, and G. B. Kenney, "The Dynamics of International Competition in the Automotive Industry. Part I: A Framework for Analyzing the Dynamics of Intermaterial Competition," Submitted for publication to Materials and Society, January, 1981

(9) G. B. Kenney and J. P. Clark, "The Dynamics of Intermaterial Competition in the Automotive Industry. Part II. A Cast Study of the Demand for Magnesium," Submitted for publication to Materials and Society, January, 1981.

Presentations

(1) J. P. Clark and G. B. Kenney, "A Framework for Analyzing the Dynamics of Intermaterial Competition in the Automotive Industry," Presented to the 71st AIChE Conference, November 1978.

(2) G. B. Kenney, "Magnesium: An Assessment of Current Trends," Presented to the Executive Committee of the International Magnesium Association, New York, N.Y., March 1980.

(3) G. B. Kenney, M. C. Flemings, and D. R. Sadoway, "An Analysis of Existing and Proposed Magnesium Primary Production Technologies," Presented to the 109th AIME Annual Meeting, Las Vegas, Nevada, February 1980.

3. TECHNOLOGY ASSESSMENT OF ELECTROLYTIC MAGNESIUM PRODUCTION AND RECOMMENDATIONS FOR RESEARCH AND DEVELOPMENT

3.1 REVIEW OF CURRENT ELECTROLYTIC PROCESSES

3.1.1 Introduction

Electrolysis of magnesium chloride is the predominant method of production of magnesium metal and accounts for approximately 72 percent of the Western world's production, plus the entire production of the Soviet Union. Major producers of electrolytic magnesium are Dow Chemical Company, NL Industries*, and American Magnesium in the U.S. and Norsk Hydro in Norway.

Electrolytic production of magnesium can conveniently be divided into two parts: cell feed preparation and electrolysis. Detailed production costs are not disclosed by magnesium producers; however, a general cost breakdown has been estimated and is shown in Table 3.1.1(1). These data show that lowering the cost of cell feed production, which represents 47 percent of the total cost of magnesium metal production, offers significant potential savings. In the course of preparation of the electrolyte, to be discussed in Section 3.4, the dehydration stage is the most complex and costly. The other primary area for high potential savings is cell design, where innovation would result in higher productivity with lower energy consumption all at a lower capital cost.

3.1.2 Cell Feed Preparation

Methods for producing anhydrous cell feed materials for magnesium chloride electrolysis may be divided into those starting from hydrated

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* NL Industries has sold its magnesium plant at Rowley, Utah, to AMAX Specialty Metals.

TABLE 3.1.1

Distribution of Costs for the Electrolysis Stage in the Electrolytic Production of Magnesium Metal (1)

Cost Elements	Percentage
Capital	25
Cell Feed Material	47
Energy	19
Personnel	4
Maintenance	5
Total	100

chlorides and those involving direct chlorination of MgO.(2) The choice is dictated by available raw materials. The most recently initiated methods are based on dehydration of magnesium chloride derived from brines and the waste products of potash and soda industries. Dehydration to the tetrahydrate of magnesium chloride is simple; dehydration below the dihydrate, however, is not. Appreciable MgOHCl, MgO, and water can form. In principle, this can be avoided by heating the dihydrate in an environment of (a) KCl to produce artificial carnallite, (b) NH_4Cl to produce ammonium carnallite, (c) dry HCl to directly suppress hydrolysis(3), or by heating hydrated magnesium chloride dissolved in a polar organic solvent.(4)

The newer production facilities, such as those of NL Industries (see Figure 3.1.1(5) and Norsk Hydro (see Figure 3.1.2),(6,7) have focused on variations of method (c), directly suppressing hydrolysis and rechlorinating residual MgO by heating in the presence of dry HCl. Previously, anhydrous magnesium chloride cell feed was produced by the chlorination of MgO, as, for example, at the old Norsk Hydro facility (see Figure 3.1.3)(7). Alternatively, Dow Chemical Co. completes the dehydration of $MgCl_2$.1-1/2 H_2O by electrolysis in the production cell.(2,8)

In the direct chlorination of magnesium oxide, the starting material is prepared by several methods which strongly depend on the raw material(2,3,8,)

a) calcination of natural, low impurity magnesites, particularly those with low silica contents;

b) calcination of magnesium hydroxide, prepared from the precipitates resulting from the combination of aqueous solutions of $MgCl_2$, including seawater and high purity limestone of dolomite;

c) calcination of magnesium carbonate prepared from $Mg(OH)_2$ derived from magnesite or from seawater.

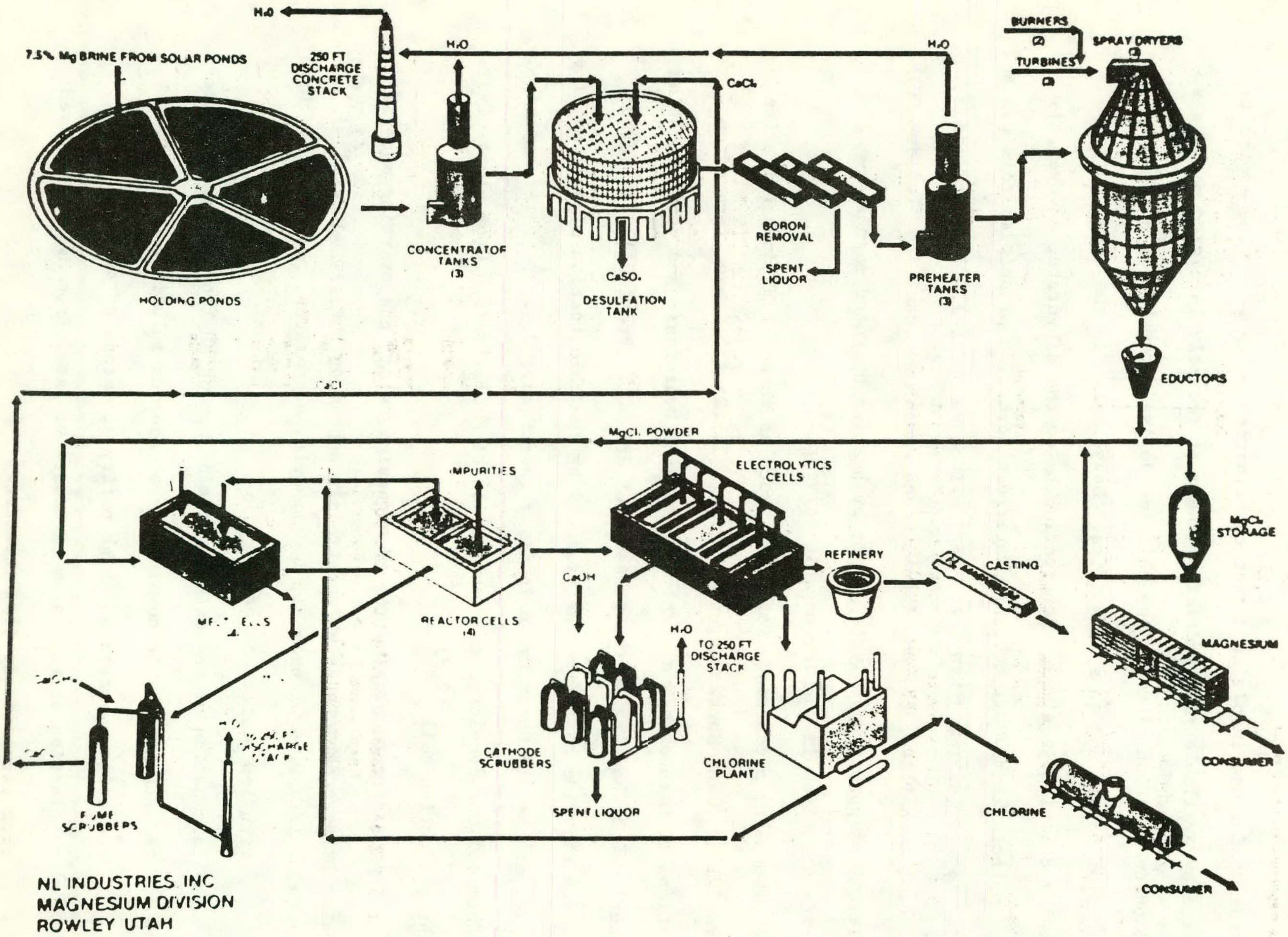

Figure 3.1.1: NL Industries Electrolytic Magnesium Process.(56)

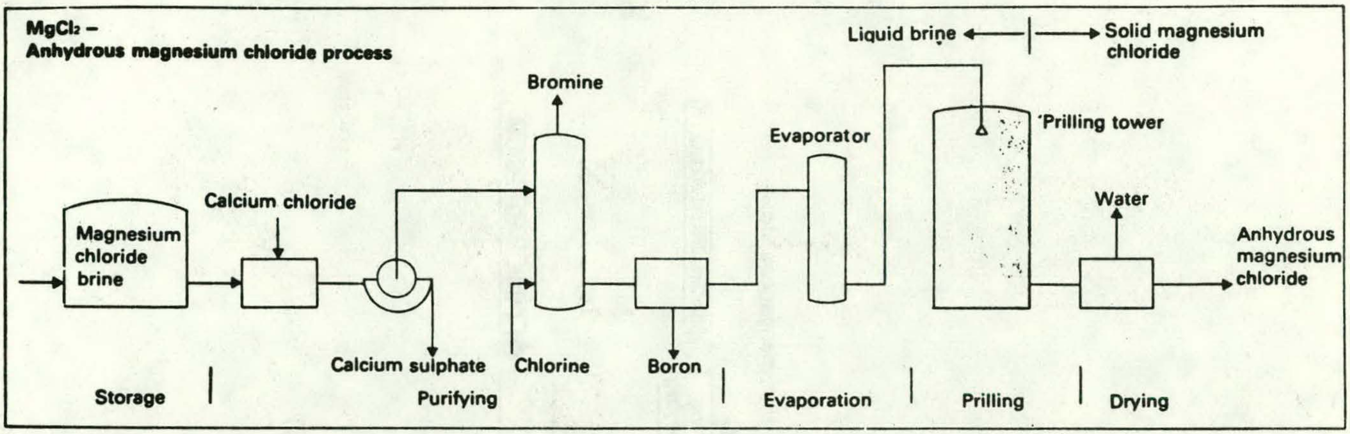

Figure 3.1.2(a): Norsk Hydro's Electrolytic Magnesium Process - Production of Anhydrous $MgCl_2$ Feed for Electrolysis Cells.(55)

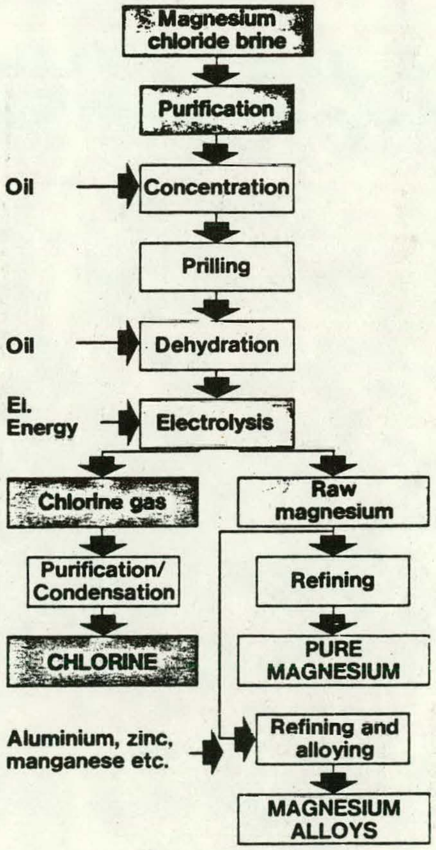

Figure 3.1.2(b): Norsk Hydro's New Electrolytic Magnesium Process - General Flowsheet.(54)

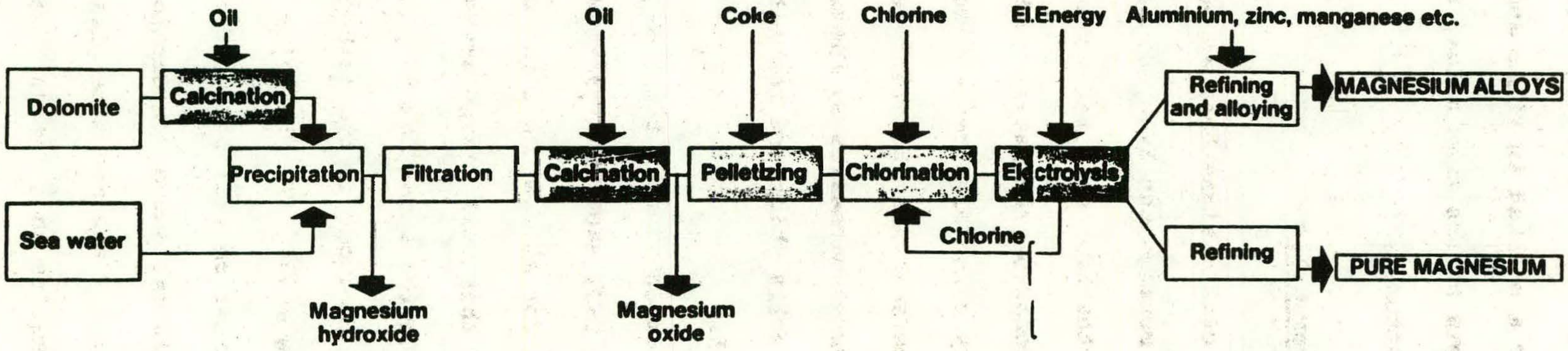

Figure 3.1.3: Norsk Hydro's Old Electrolytic Magnesium Process.(54)

Chlorination of the magnesium oxide is performed in a shaft furnace in the presence of carbon. Pellets consisting of MgO, coal, and peat with $MgCl_2$ solution as binder are coked in kilns and then fed into the top of the chlorinator. Chlorine gas enters from below, and the molten $MgCl_2$ is tapped periodically from the bottom.

3.1.3 Electrolyser Cells

Two electrolytic cell designs have accounted for most of the world's production of magnesium metal: the I.G. cell and the Dow cell. The general construction of the I.G. cell is shown in Figure 3.1.4.(2,3,9,10) Carbon anodes are positioned between steel cathodes. Diaphragms (partitions) constructed of refractory materials are immersed into the electrolyte between each anode and cathode to separate the chlorine from the metal product in order to prevent the loss of magnesium by chemical reaction. There is no external heating of the cells which are insulated with refractory brick and contained in a steel tank.

The approximate composition of the I.G. cell electrolyte derived from chlorinated MgO is $CaCl_2$-40%, NaCl-30%, KCl-20%, and $MgCl_2$-10%.(2) Typical performance data for an I.G. cell are displayed in Table 3.1.2.(2,11)

The advantages of this cell design are as follows. Cathode current efficiencies are high (figures exceeding 90 percent are not uncommon). While magnesium metal is being produced at the cathode, dry chlorine of commercial purity is produced at the anode. The chlorine must be kept away from the metal or chemical recombination will occur. The low water content of the electrolyte results in minimal anode consumption, and thus less downtime for labor intensive servicing. There are some disadvantages of this cell design. The refractory spacers require that the cathode-anode separation be relatively

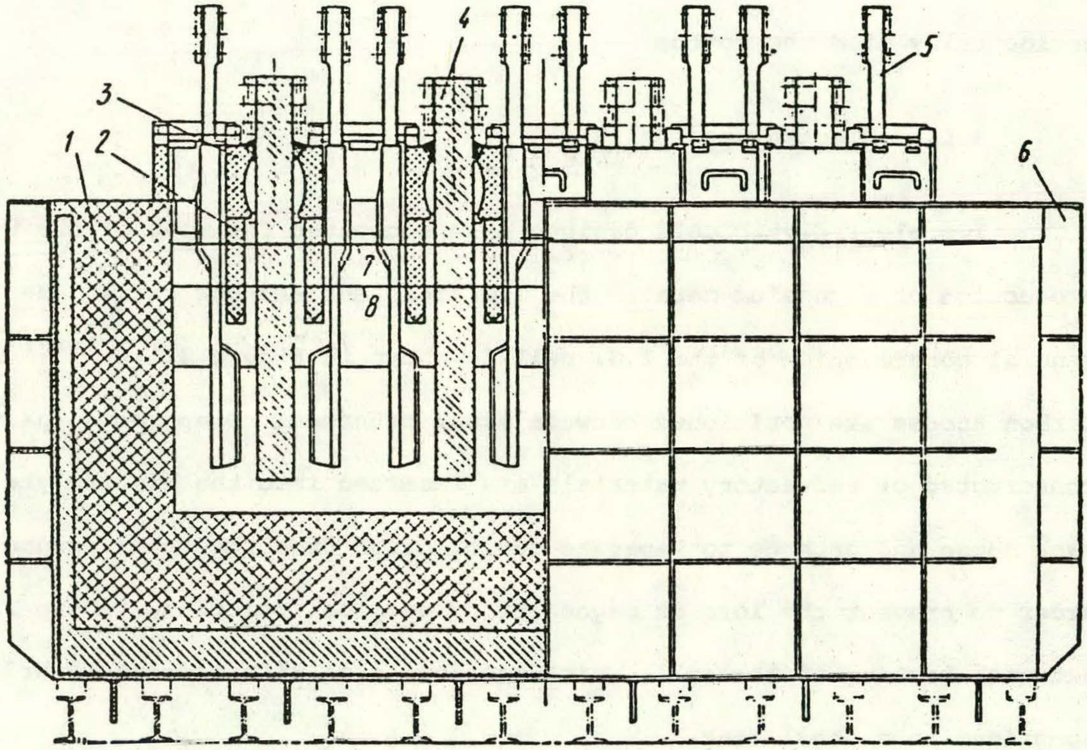

Figure 3.1.4: The I.G. Cell. 1 - lining, 2 - diaphragm, 3 - anode hood, 4 - anode, 5 - cathode, 6 - jacket, 7 - upper level of electrolyte, 8 - lower level of electrolyte.(53)

TABLE 3.1.2

Typical Performance Data for an I.G. cell(2,11)

Operating temperature	740°C
Cell voltage	5-7 volts
Current	18,000-150,000A
Approximate current density	0.35-0.5 A/cm^2
Current efficiency	80-90%
Energy efficiency	30-35%
Energy consumed	15-18 kWh/kg
Anode graphite consumption	0.02 kg/kg Mg
Daily metal output per cell	Approx. 200 kg

wide, resulting in a large iR drop across the electrolyte and severely limiting the current density at which the cell may be operated. Ultimately, the spacers fail, and the cell must be shut down for repair. Furthermore, metal must be collected from each of many small compartments.

The processes of NL Industries and the older Norsk Hydro facility use modified I.G. cells. Both producers have introduced changes. NL mentions the addition of fluoride ions to the electrolyte.(12) The newer Norsk Hydro process at Porsgrunn (Figure 3.1.2) uses diaphragmless cells, where the magnesium metal and the chlorine are isolated from one another by the circulation of the electrolyte. To reduce maintenance costs, Norsk Hydro have developed a replaceable cathode unit as part of a modular cathode system.(13)

As noted earlier, in the Dow process(14) the cell feed is incompletely dehydrated with an average composition of $MgCl_2 \cdot 1.7H_2$. The flow diagram for the Dow seawater magnesium process is shown in Figure 3.1.5. The electrolyte composition for the Dow cell is estimated to be approximately $NaCl$-57%, $CaCl_2$-20%, $MgCl_2$-20%, KCl-2%, CaF_2-1%.

A sectional diagram of the Dow cell is shown in Figure 3.1.6. The cells consist of externally heated steel pots 5 ft wide, 6 ft deep and 13 ft long. Cylindrical graphite anodes 9 inches in diameter and 9 ft long are suspended through an arched refractory cell cover. The pot acts as the cathode. Temperature is maintained by gas firing. The water in the cell feed usually flashes off immediately. However, the hydrous nature of the cell feed causes heavy anode wear, and the anodes require daily adjustment. Typical performance data for the Dow cell are given in Table 3.1.3.

The Dow cell has the following advantages. The external heating allows more choice in ampere loads and even complete power interruption for extended periods. The use of conical cathodes with a system of inverted

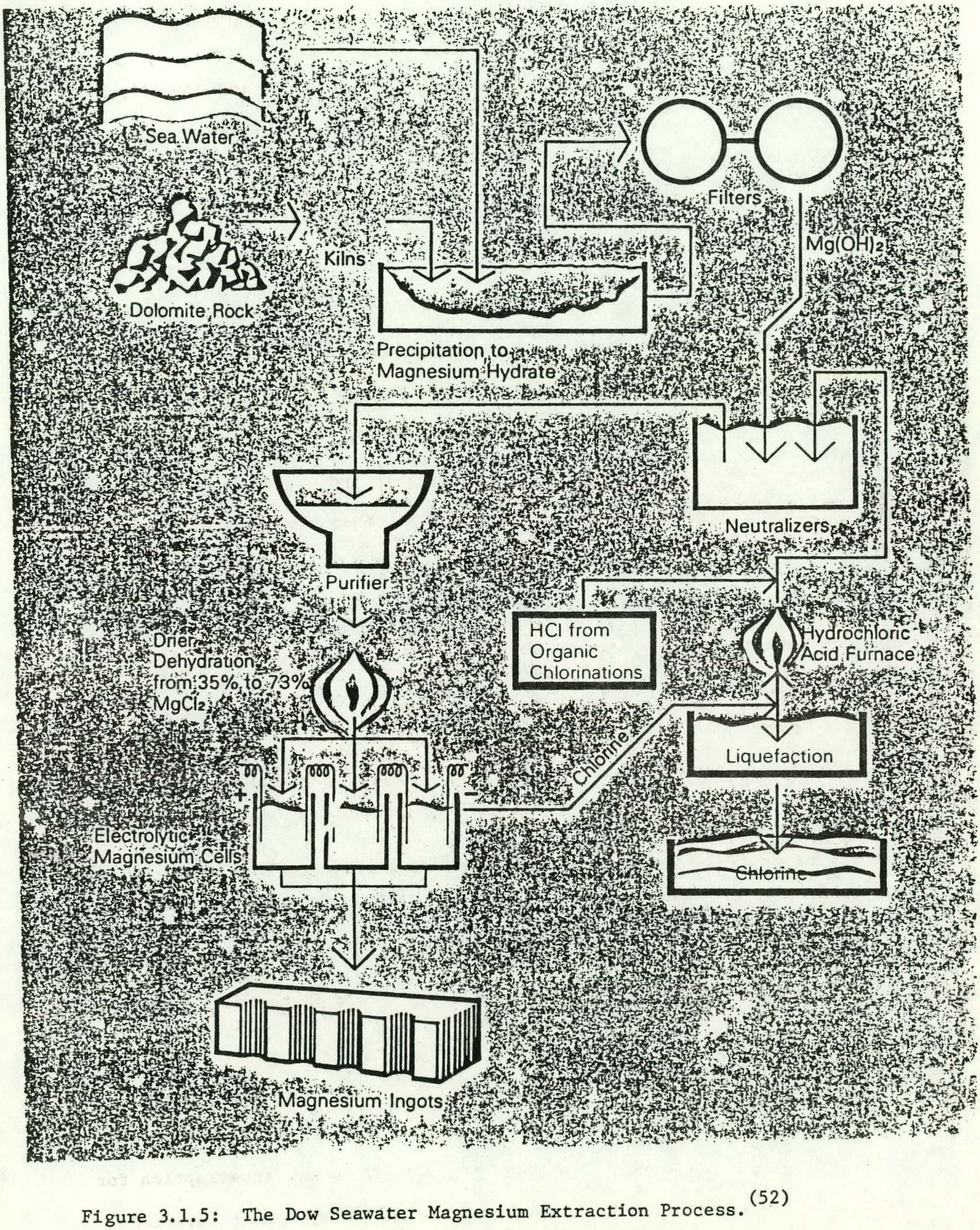

Figure 3.1.5: The Dow Seawater Magnesium Extraction Process.[52]

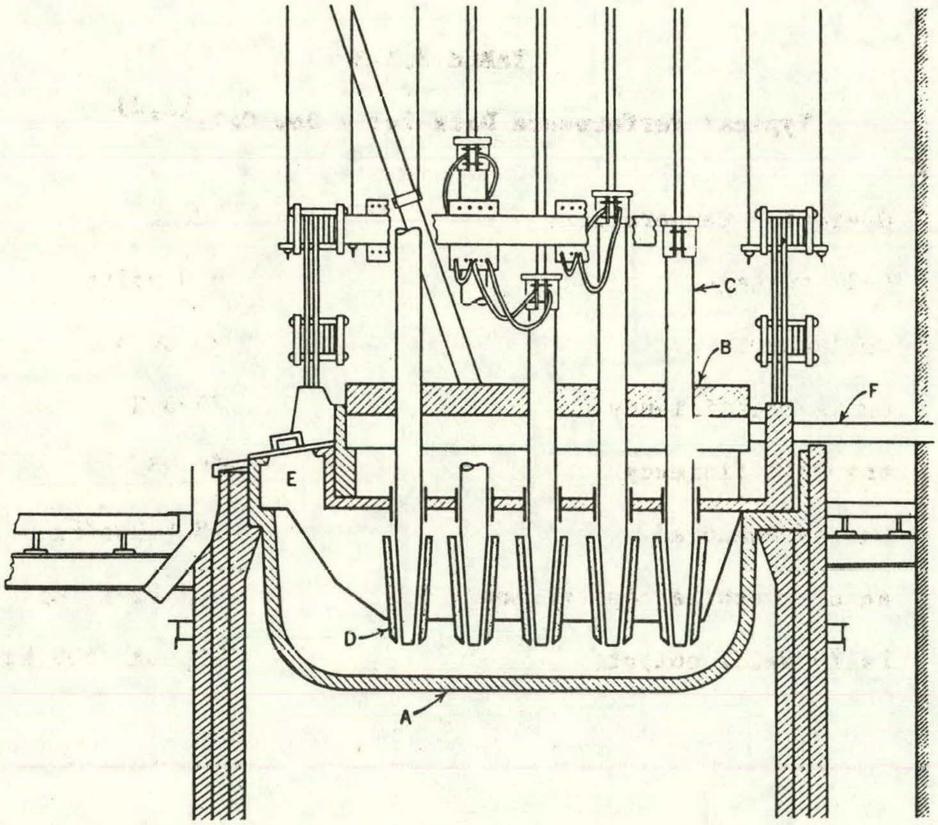

Figure 3.1.6: The Dow Magnesium Cell. The steel container (A) is equipped with ceramic cover (B) through which pass graphite anodes (C). The magnesium is deposited on the cathodes (D) and is diverted as it rises into collection sump (E). The chlorine is withdrawn through vent (F).(51)

TABLE 3.1.3

Typical Performance Data for a Dow Cell(1,2)

Operating temperature.	700°C
Cell voltage	6.0 volts
Cell current	90,000A
Current efficiency	75-80%
Energy Efficiency	30-35%
Energy consumed	18.5 kWh/kg
Anode graphite consumption	0.1 kg/kg Mg
Daily metal output	Approx. 500 kg

troughs to trap rising magnesium and isolate it from the chlorine permits close cathode-anode spacing and, as a consequence, operation at higher current densities without overheating. However, final dehydration of feed inside the electrolysis cell results in high anode consumption and the attendant servicing. In addition, contamination of the chlorine with water vapor and HCl renders it unmarketable. However, improvements continue to be made. In a recently granted patent(15) metallic molybdenum and tungsten or inorganic salts of these metals are added to the electrolysis cells to reduce sludge formation and increase cell efficiency.

Dow has also patented an electrolytic process which uses a lithium chloride based electrolyte which is less dense than magnesium (16). In these cells, magnesium sinks to the bottom of the bath much as aluminum does in its conventional industrial cells. The high cost of lithium chloride as a reagent plus its strong affinity for water have made such a process not commercially attractive in this country.

Magnesium is also produced by a third cell type: a diaphragmless cell originally developed by Alcan about 25 years ago(17) but recently redesigned for much improved performance and higher operating currents.(18,19) Diaphragmless electrolyser cells contain a larger fraction of the electrolyte within the inter-electrode working volume. The resulting increased electric current density leads to an increased yield of magnesium metal for a given cell size, reduced specific heat losses, and a smaller specific energy expenditure. Although Alcan ceased magnesium production in 1958, the cells are still operated by some titanium producers such as Osaka Titanium Co. in Japan and Oregon Metallurgical Corp. in the U.S. for their recycling of byproduct anhydrous magnesium chloride to obtain chlorine and magnesium, the latter for use in the reduction of titanium tetrachloride. Alcan itself does not produce magnesium, being an aluminum producer foremost. Complex corporate strategy dictates that it should license the process to others at the moment. However, the company continues to support magnesium research in order to keep its technology competitive.

The situation is almost the same with another large aluminum producer, Alcoa, which does not itself produce electrolytic magnesium but continues to apply for patents which govern the production of the latter(20,21). Indeed the patent for the new Alcoa smelting process for the production of aluminum in chloride melts cites magnesium as well(22).

Detailed information about the electrolyser cells currently being operated by magnesium producers is sparse. It is known, however, that in the U.S. among the producers using anhydrous cell feed, NL Industries operates IG-type cells and American Magnesium operates diaphragmless cells, the design of the latter having been licensed from the USSR.(23,24) In addition to IG-type cells,(11) it is believed that Norsk Hydro also uses a diaphragmless cell which has evolved from the design described in their 1975 patent.(25) Table 3.1.4 gives the operating characteristics of some common electrolyser cells.

3.1.4 CURRENT AND ONGOING RESEARCH

Electrolysis of magnesium chloride is the predominant method of production of magnesium metal, accounting for approximately 72 percent of the Western world's production and the entire production of the Soviet Union. Major magnesium producers employing the electrolytic process include Dow Chemical, NL Industries, and American Magnesium in the U.S. and Norsk Hydro in Norway.

Current and ongoing research by the major producers and other groups is reviewed.

TABLE 3.1.4[1,11]

Operating Characteristics of Common Electrolysis Cells

Cell Type	Cell Current (kA)	Current Efficiency (%)	Voltage (volts)	Specific Energy (kWh/kg)
Alcan Cell	80	90-93	5.7-6.0	14
IG-Cell	150	80-85	5.5-7.0	15-18
Diaphragmless (Soviet)	200	85-90	5.0-6.0	13-15
Norsk Hydro (New)	250-350	92-93		12-13

DOW CHEMICAL CO., Freeport/Velasco, Texas

Dow produces more than 40 percent of the world's magnesium. The facility in Texas has been in operation for over 35 years, currently using a combination of two raw materials, seawater and dolomite. Over the years, Dow has modified and improved its process. In addition, periodic announcements have been issued regarding a totally new technology which Dow claims will operate at a 50 percent reduction in energy consumption compared to 1975. A demonstration unit will soon be built.

NL INDUSTRIES, INC., Rowley, Utah*

NL industries decided to enter into the production and marketing of magnesium in 1964, commenced plant construction in 1969, and began operations in 1972. After operating at a substantial financial loss, the firm suspended operations early in 1976, and with technical assistance from Norsk Hydro made major modifications to the process and equipment. Operations were resumed in March 1977, and the facility is currently producing at the rate of 25,000 tons annually.

AMERICAN MAGNESIUM, Snyder, Texas

In 1968, American Magnesium started construction of a magnesium plant for production of 10,000 tons/year of magnesium and 20,000 tons of chlorine. The plans were to expand to 20,000 to 30,000 tons per year of magnesium based on local magnesium chloride brine wells. The first metal was produced in 1969. Start-up difficulties coupled with an electrical fire closed the plant in 1971. The facility remained closed until 1974. During the extended

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* NL Industries sold the Rowley magnesium facility to AMAX in 1980. At the time of the announced sale, AMAX revealed that it plans to increase production to 45,000 tons/per year.

shutdown Soviet cell technology was licensed. Although no direct information is available, it is suspected throughout the industry that the cells are diaphragmless and large, operating at over 100,000 amperes.

ALUMINUM COMPANY OF CANADA Ltd. (Alcan), Arvida, Quebec

The Alcan-type magnesium cell was developed in the 1940's. Continuous improvements have been made to the 40 kA design which had been in operation for close to 25 years. In 1971 a research program using an air/water model cell was undertaken to optimize current efficiency, voltage drop, and life expectancy in terms of anode/cathode configuration. Additional laboratory studies were conducted at the University of Newcastle, NSW, Australia.

These studies led to a redesigned cell intended to operate at 120 kA. However, for experimental purposes an 80 kA model in February 1975 was installed at Osaka Titanium and has been operated cooperatively by both companies. Higher performance than expected was achieved in energy savings, sanitary working conditions, and reduced environmental pollution.

OSAKA TITANIUM COMPANY, Amagasaki, Japan

In 1961, Osaka Titanium licensed Alcan magnesium cell technology. The former company made many improvements, increasing the production rate of magnesium by boosting the current from the original 26 kA to 40 kA. Since 1975, Osaka has been operating the new 80 kA Alcan cell in cooperation with Alcan, achieving higher performance than expected.

ALUMINUM COMPANY OF AMERICA, Pittsburgh, Pennsylvania

It has been suggested that the newly developed aluminum chloride electrolytic cell could be modified to give a more efficient magnesium chloride cell. Indeed, the ALCOA patent on their new aluminum chloride cell covers magnesium production.

NALCO CHEMICAL COMPANY, Oak Brook, Illinois

A paper presented by a Nalco Chemical Company representative at the 1979 Annual Meeting of the International Magnesium Association and two earlier patents describe a technology to extract magnesium chloride from virtually any brine by an organic chemistry process. Nalco uses over 10 million pounds of magnesium annually to produce tetraethyl lead, discharging all of this as a 3 percent magnesium chloride aqueous solution. The new technology will allow Nalco to reclaim the magnesium chloride from this waste stream. In pilot plant operations magnesium chloride containing less than 500 ppm total impurities has been produced from 35 percent magnesium chloride brine obtained by solar evaporation from the Great Salt Lake. Similar results have also been achieved from other brines with much higher levels of impurities.

NORSK HYDRO, Porsgrunn, Norway

Starting in 1951 with an annual production of 266 tons, Norsk Hydro is now the second largest producer of magnesium in the Western world with an annual production capacity of 55,000 tons. Norsk Hydro begins with three raw materials: dolomite, seawater, and brine. Magnesium hydroxide precipitate is calcined to magnesium oxide which is then chlorinated to magnesium chloride feed for the electrolysis cells. Anhydrous magnesium chloride is also made directly by concentration and dehydration of magnesium chloride brine. New high current diaphragmless electrolyser cells have been developed using laboratory simulations. Research and development remain active as process improvements are sought in the light of plant data.

Norsk Hydro has close ties with the Technical University of Norway in Trondheim where research in its Institute of General and Inorganic Chemistry is centered on light metals (Al, Mg, and Ti), rare earths, catalysis, membrane chemistry, and fundamental studies on complexation in liquid and gas systems. Over the past few years a major project on the dynamics of magnesium electrolysis has been examining the elements of the back reaction between magnesium and chlorine in industrial electrolysis of magnesium chloride. Measurements have been made of chlorine and magnesium solubilities in magnesium chloride, surface and interfacial tensions, wetting angles and electrolytic separation of liquid magnesium, diffusivities of dissolved chloride and the degree of magnesium dispersion, and magnesium diffusivities in chloride melts.

SOVIET UNION

Research and development in magnesium processing are being conducted at a number of institutions in the USSR, the most prominent being the All-Union Aluminum and Magnesium Institute, Leningrad. Most recently published work focuses on cell design optimization: bottom lead-in cathodes, larger anodes, channeled anodes, etc. It is generally believed in the industry that Soviet cell technology is among the most advanced in the world, but that their cell feed preparation, i.e. dehydration technology, needs improvement.

3.2. RAW MATERIALS

Magnesium is one of the most abundant elements, comprising 2 percent of the earth's crust. Electrolytic magnesium comes from magnesite, dolomite, carnallite, and from magnesium chloride contained in seawater, lake water, brines, and in the wastes of the potash and soda industries. The compositions of some magnesium minerals, seawater, and a number of brines are shown in Tables 3.2.1 and 3.2.2, respectively.(2,3) Obviously the use of a magnesium

TABLE 3.2.1

Composition of Magnesium Minerals Most Commonly Used for Magnesium Production(3)

Mineral	Chemical Formula	MgO	Mg
Magnesite	$MgCO_3$	47.8	28.8
Dolomite	$MgCO_3 \cdot CaCO_3$	21.8	13.2
Bischoffite	$MgCl_2 \cdot 6H_2O$	19.9	12.0
Carnallite	$MgCl_2 \cdot KCl \cdot 6H_2O$	17.8	8.8

TABLE 3.2.2

Composition of Brines and Sea Water(3) (weight percent)

Salt	Sea Water	Great Salt Lake Brine (1955)	Dead Sea Brine	Bocana de Viri Pern, Brine
KCl	0.04	1.45	0.66	1.49
NaCl	1.40	12.90	4.65	13.29
$CaCl_2$	0.12	0.12	5.06	0.12
$MgCl_2$	0.26	3.76	15.66	16.87
$MgSO_4$	0.33	7.56	0.13	9.03
Total Dissolved Solids	2.15	25.8	26.2	40.8
Mg	0.14	2.49	4.03	6.13

chloride raw material eliminates processing steps such as calcination and chlorination. Since potassium salts are produced on a large scale at many places throughout the world, the volume of magnesium chloride liquor available as a byproduct is very large. The liquors can contain as high as 33 percent $MgCl_2$.

Depending on the raw material, preparation of the anhydrous magnesium chloride for feed to the electrolytic cell can involve a great variety of processes. For example, in their old process Norsk Hydro used raw materials in the following approximate proportions: seawater 41 percent, dolomite 46 percent, and magnesium chloride brine 13 percent.(6) Anhydrous magnesium chloride suitable for electrolysis is produced by chlorination of the magnesium oxide resulting from calcination of the magnesium hydroxide precipitating from a combination of the dolomite and seawater.* On the other hand, the new Norsk Hydro process and the processes of NL Industries and American Magnesium are based entirely on the evaporation and dehydration of magnesium chloride liquors or brines.(5,6,10,26-30)

In view of the increasing demand for potassium fertilizers and their increasing production volume from potassium-magnesium mineral sources, the problem of disposal of strongly polluting magnesium chloride liquors has become acute. When potassium sulfate fertilizers are produced from potassium-magnesium minerals, decomposition of the waste product yields magnesium chloride liquors with 24 to 33 percent $MgCl_2$. For example, the composition of the magnesium chloride liquor waste from the potash production

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* The Dow process, although not based on anhydrous magnesium chloride, also uses cell feed produced from the chlorination of magnesium hydroxide precipitate resulting from the combination of the two raw materials, seawater and dolomite (see Section 3.1.2).

of Kali and Salz AG, which is used as the raw material for the new Norsk Hydro process, is shown in Table 3.2.3.(28)

Since the major producers using anhydrous magnesium chloride as the cell feed all currently begin with natural brines or by-product liquors, further discussion of the process components of the electrolytic production of magnesium will be restricted to these raw materials. The reduced complexity (and cost) of producing the anhydrous magnesium chloride from these raw materials is a primary consideration in planning for increased production of metallic magnesium. In addition, the coproduction of 2.8 tons of chlorine per ton of magnesium produced provides a strong economic incentive, since this gas may be recycled to the dehydration step.

3.3 EVAPORATION OF BRINES

Brines are first processed by evaporative separation of $CaSO_4$, NaCl, $MgSO_4$, KCl, and carnallite, in that order. The procedure may be carried out in-plant or by solar evaporation either in discrete basins or in a continuous flowing system.(29) For example, in the three solar-pond system operated by NL Industries at the southwest Great Salt Lake, Utah, about 70 percent of the sodium chloride content is precipitated in the first pond.(5,26,27) After transfer of the effluent to the second pond, about 30 percent additional sodium chloride value is precipitated as well as some potassium values. In the third pond, the magnesium content is increased and additional potassium values are removed, largely as the mineral kainite ($KCl \cdot MgSO_4 \cdot 3H_2O$). The typical composition of the concentrated brine produced by NL Industries in their solar ponding system is shown in Table 3.3.1. At this stage, the magnesium content is approximately 7.5 percent.

An experimental two-year solar ponding cycle is currently being

TABLE 3.2.3

Composition of Magnesium Chloride Liquor Waste Product from Kali and Salz AG(28)

Weight Percent or * ppm	
$MgCl_2$	33
$MgSO_4$	1.7
NaCl	0.5
kCl	0.2
MgO	0.01
CaO	0.01
Br	0.04
Fe	1*
B	15*
Cu	10*

TABLE 3.3.1

Typical Composition of Effluent from Three Solar Pond System of NL Industries at the Great Salt Lake(5,26)

	Weight Percent
$MgCl_2$	26.00
KCl	1.72
NaCl	1.44
$CaSO_4$	0.85
LiCl	0.55
$Na_2B_4O_7$	0.14
$MgSO_4$	4.26
H_2O	65.04

operated by James Macey at a northwest location on the Great Salt Lake in a single mud-walled basin with a length to width ratio averaging 80 to 1.(31) The solutions are continuously moving, dropping out crystals of salt and the less soluble chemicals as they go. The magnesium chloride concentrate produced is transferred to a holding pond. Depending to a small extent on variations in the weather and possible pond bottom leakage, the composition of the product is approximately 36 percent $MgCl_2$, 2 percent $MgSO_4$, no more than 1 percent other chlorides, and the balance water. In the case of the brine from the Great Salt Lake, a two-year cycle increases the lithium chloride concentration, which is desirable since this increases the electrolyte conductivity.

3.4 PURIFICATION

Impurities in the raw materials can have significant effects both on the preparation of the anhydrous magnesium chloride cell feed and on the electrolysis itself. Of particular concern are the presence of sulfates and traces of boron, both of which can severely reduce electrolysis yields.(3,10)

In general, sulfates are removed as calcium sulfate, precipitated by the addition of calcium chloride to the magnesium chloride bittern derived from a solar ponding operation or potash waste liquor. Boron is eliminated by various solvent extraction techniques.

It may be necessary, depending on the brine composition and the required final composition of the cell feed, to remove additional potassium values. NL Industries precipitates carnallite in an additional step in their purification procedure.

An attractive technique which has not been demonstrated on an industrial scale is the use of solvent extraction by ethylene glycol both to purify and to dehydrate. In a series of patents(32-34) Nalco Chemical Company describes the treatment which includes boron removal and recycling the ethylene glycol by reacting the latter with ammonia.

3.5 DEHYDRATION

3.5.1 Theoretical Principles

The dehydration of magnesium chloride is non-trivial as the water is chemically bound in the form of hydrates. (In addition to the hexahydrate, $MgCl_2.6H_2O$ (bischoffite), the tetrahydrate, dihydrate, and monohydrate exist.) Simple heating to temperatures above water's normal boiling point, even in vacuum, will not suffice, and, indeed, in certain cases will result in the formation of undesirable compounds which are more difficult to reduce than the hydrates themselves. In particular, simple heating to dehydrate below 2 moles of water is counterproductive; there is considerable hydrolysis resulting in the formation of MgOHCl.

Thus, the operation is conducted in an atmosphere of HCl maintained at a sufficiently high partial pressure. Furthermore, if air is not excluded, the reaction of oxygen with solid $MgCl_2$ at temperatures above about 500 K will result in the formation of MgO by the reaction

$$MgCl_2 + 1/2\ O_2 = MgO + Cl_2.$$

3.5.2 Current Technology

Bischoffite is commercially dehydrated in a variety of ways. Usually, the hexahydrate is heated in air to 200°C to produce a material containing approximately 1-1/2 moles of water per mole $MgCl_2$. This mixture of mono- and dihydrates is then heated to a higher temperature in an atmosphere of HCl to complete the dehydration.

Both American Magnesium and NL Industries use spray dryers to dehydrate the concentrated magnesium chloride brine.(5,27,29) The flow diagram of the dehydration process used by NL Industries is shown in Figure 3.1.1.(35) The purified $MgCl_2$ solution is concentrated in-plant to a composition of approximately 41 percent $MgCl_2$, 4 percent additional solids, and 55 percent H_2O. Three spray dryers in series each 38 feet in diameter yield a dehydrated $MgCl_2$ powder product containing a maximum of 5 percent H_2O and 5 percent MgO. A typical analysis of the spray dried magnesium chloride is given in Table 3.5.1.(5,26)

A unique procedure is used by NL Industries in supplying heat to the spray dryer operation. The facilities are designed so that about 80 megawatts of power are generated by gas turbines burning natural gas. As indicated in Figure 3.1.1, the hot exhaust gases from the gas turbines furnish the heat necessary for spray drying.

Since cell feed containing as much as 5 percent MgO and 5 percent H_2O is unacceptable to the IG cells used by NL Industries, another operation is needed to reduce the content of MgO and H_2O. A simple method would be to melt the sprayed product, let water and HCl flash off, precipitate the MgO and use the supernatant.(36) However, perhaps because of losses, this approach has not been applied. Instead, the sprayed product is melted and chlorinated with HCl gas. NL has also patented a process in which spray-dried $MgCl_2$ is purified by fusing the salt and bubbling chlorine gas through the melt in the presence of carbon and an iron-chloride complex(37).

Conventional chlorination is limited by the fact that some of the

TABLE 3.5.1

Typical Composition of Spray Dried Magnesium Chloride(26)

		Per Cent
Magnesium Chloride	$MgCl_2$	81.52
Potassium Chloride	KCl	1.08
Sodium Chloride	$NaCl$	1.50
Calcium Chloride	$CaCl_2$	3.07
Calcium Sulfate	$CaSO_4$	0.50
Lithium Chloride	$LiCl$	1.86
Sodium Tetra Borate	$Na_2B_4O_7$	0.47
Magnesium Oxide	MgO	5
Water	H_2O	5

reactants and products will attack the container. Alcoa holds a patent(21) which names nitride based materials, such as silicon oxynitride, as increasing the useful furnace life and reducing contamination of the product salt as well.

The Soviets have proposed using HCl gas or phosgene ($COCl_2$) to chlorinate the magnesium chloride melt to which has been added a reactive type of carbon (e.g., petroleum coke) in a finely divided form.(3) In addition to converting MgO back to the chloride, chlorination has the additional benefit of purification. However, there still may be impurities other than sulfur and boron, such as iron, manganese, titanium, and bromine, which are not removed even by a purification process as extensive as that practiced by Norsk Hydro, or which may have been introduced during the processing. Carbochlorination will purify the melt of many such impurities.

The Norsk Hydro new dehydration process is shown schematically in Figure 3.1.26. In this process the first stage of evaporation is carried out in standard dryers, producing a hydrate having 4.0 - 5.8 moles of H_2O per mole of $MgCl_2$.

Prilling, used extensively by the fertilizer industry, is a process in which the melt is centrifuge-sprayed or sieved-plate sprayed to form droplets which are converted into solidified spheroidal grains by cooling in a gaseous or liquid medium. Large prills, 2 - 4 mm in diameter, are most easily produced by sieved-plate spraying in a counter current of air in a 25 m high tower. Relatively small prills, 0.5 - 2 mm in diameter, have been produced using air disintegration of a brine jet. These prills are free flowing and may be stored in tanks without lumping. The relatively large size of the prills compared with the spray dried product, where the particle size is mostly less than 15 microns, acts to prevent losses in the form of dust which is carried away by the drying gas, and of which a great part cannot be recovered economically. However, the dust losses are somewhat reduced in the spray drying system described previously (see Figure 3.1.1) by returning the dust from the cyclone gas to the input brine.

Strict control of the brine temperature at slightly above the temperature at which initial solidification occurs is required. In practice, the discharge temperature depends on the degree of hydration and the purity of the brine. Brine with less than four moles of water is difficult to prill because solid material starts to precipitate. On the other hand, when the moisture content is higher than the hexahydrate, difficulties are likely to arise due to lumping of the prilled product.

The prills of magnesium chloride can be dehydrated to form anhydrous magnesium chloride by known drying methods. Norsk Hydro prefers fluidized bed drying or shaft kiln drying, the latter being particularly suited to 4 - 6 mm prills. The magnesium chloride prills are dehydrated to approximately 2 moles of H_2O in air, and final dehydration is performed at a higher temperature in HCl gas. The number of dehydration stages in HCl gas depends on the allowable MgO and H_2O contents in the final product. Normally three stages or more would be required if a substantially anhydrous product is desired containing less than 0.2 percent MgO.

A Norsk Hydro patent reports on a series of drying tests.(38) Although the process yields a salt containing low water and oxide, the treatment times are long. The diffusion of water to the surface of the relatively large diameter prill is rate limiting. To its credit the new process is essentially a closed system, and the environment in the plant is reportedly quite good. Also, effluents from the plant are significantly reduced: off-gases are scrubbed in two stages to remove the hydrochloric acid, which is discharged at a maximum of 1 kg HCl/hr. This compares with the limits for effluents from the older plant of 130 kg chlorine/hr. The flue gases from the oil heating system are scrubbed in seawater to remove sulfur dioxide and discharges of chlorine, bromine, and dust are negligible.

At full production, the new Norsk Hydro plant will supply about 65,000 tons of anhydrous magnesium chloride per year. This amount of cell feed can be used to produce approximately 15,000 tons of magnesium metal.

Other methods of dehydration used or considered by production facilities in the Soviet Union are described by Strelets.(3) These for the most part include spray drying, fluidized bed drying, and combinations of the two. To avoid the complexities associated with the dehydration of magnesium chloride, methods based on the dehydration of ammonium carnallite $MgCl_2.NH_4Cl.6H_2O$(3,31) have been devised.

Briefly, ammonium carnallite is made from solutions of magnesium chloride and ammonium chloride; ammonium carnallite hexahydrate is dehydrated in, for example, fluidized bed furnaces; and ammonium carnallite is decomposed. Ammonium chloride vapors liberated are condensed and recycled in the manufacture of the ammonium carnallite.

Another method of producing cell feed material practiced extensively by the Soviets, which is not based on brines but is still of interest, uses carnallite, $KCl.MgCl_2.6H_2O$, as the raw material.(3) Carnallite, after preliminary processing, is dehydrated more easily, and the accompanying hydrolysis is less extensive than the case for bischoffite. The dehydration is usually carried out in two stages: the hexahydrate is converted to the dihydrate at 90°C, and the dihydrate is dehydrated at 240°C. The first and second stages of dehydration of carnallite are usually performed in fluidized bed furnaces.

Significant amounts of water and magnesium oxide remain in the product. Thus, before being fed to the electrolysis cell, the material is heated to 800° - 850°C in an electric furnace or chlorinator in order to treat the remaining water, hydroxychlorides, and magnesium oxide.

3.5.3 Modifications in the Dehydration Process Technologies

The central question to be answered here is how to suppress hydrolysis and yet remove water to levels acceptable to modern electrolysis cells. Some unconventional ideas in this regard follow.

Although magnesium is lost by solid-liquid separation, the value of the high-purity, fully-burned MgO must be considered. For example, the typical spray dried product contains somewhat less than 5 percent of MgO and 5 percent H_2O. The remaining water can be removed by superheating the melted product whereupon additional MgO will form. In order to remove the solid magnesium oxide, the melted spray dried product can be passed through a settling furnace to allow the suspended solids to settle to the bottom, and the magnesium chloride can be separated from the settled material by decanting.(38) Purification can be combined with the settling operation by, as described by Lepsoe,(29) adding a sludge from the electrolysis cell. Any metallic impurities which are present in the molten magnesium chloride and are below magnesium in the electromotive series are replaced from their respective chlorides by the metallic magnesium trapped in the cell sludge.

Following the same approach, it has been suggested that depleted cell bath be used directly to melt the dehydrated magnesium chloride, thus conserving energy.(40) Separation of the MgO from the magnesium chloride could be accomplished by settling or by mechanical devices.(41,42)

Major modifications of the dehydration process may also be considered. The methods of dehydration currently practiced are based on thermodynamics of the reactions between the hydrates of $MgCl_2$ with little regard either to the role of minor constituents or to the kinetics of the reactions.

It has been observed that in spray drying small amounts of alkali chlorides were beneficial in suppressing hydrolysis.(29,43) The dehydration of magnesium chloride solutions with 6 percent KCl and 3 percent NaCl gave approximately the same results as the dehydration of carnallite (56 percent MgCl, 44 percent KCl). Additional evidence of the potential benefits of alkali chlorides was given in a patent dealing with the destructive calcination of magnesium chloride hydrate in order to produce magnesium oxide and hydrochloric acid.(44) It was noted that KCl and NaCl concentrations must be suppressed below a total of 6 percent (in dry $MgCl_2$) or part of the product would be anhydrous magnesium chloride.

These results offer enough evidence of the beneficial effects of small alkali chloride contents during dehydration that experimental and pilot studies are warranted. These studies should determine the optimum concentrations of the alkali chloride additions and the mechanism by which they suppress hydrolysis.

There is a need for more data on the kinetics of the dehydration and hydrolysis reactions. Table 3.5.2 shows the results of some spray drying on a magnesium chloride solution where it was found that the magnesium oxide content of the product decreased with increasing spray temperature.(45) Based on thermodynamic considerations the opposite results would have been expected. Further work is needed to aid process design.

These results and others like them suggest that detailed time-temperature data of the dehydration, hydrolysis, and decomposition reactions of hydrates of magnesium chloride are required. The potential exists for performing the dehydration process under non-equilibrium conditions at much higher temperatures and for much shorter times. Specific recommendations

TABLE 3.5.2

MgO in Spray Dried Magnesium Chloride(29)

Inlet Temperature, °C	400	450	500
Exit Temperature, °C	200	250	300
MgO in spray Dried Product, wt% for 1.3 mole H_2O/mole $MgCl_2$	6.4	4.1	2.0

follow in the next section.

3.6 ASSESSMENT AND RECOMMENDATIONS

3.6.1 Critical Assessment of the Current State of the Art

Regardless of cell design, approximately half the cost of production of electrolytic magnesium is associated with dehydration of its chloride. It is clear that if electrolytic magnesium is going to be competitive, not just with respect to that produced thermochemically but in the general marketplace of structural materials, a new energy-efficient industrial dehydration technology must be developed. The greatest improvements in cell design will, in turn, be amplified by the availability of high purity electrolyte. Indeed, most of the materials degradation problems in electrolyzer cells today are a consequence of the presence of small amounts of water and oxygen in the electrolyte. Thus, even without optimizing cell design one would realize savings in the form of dramatically reduced maintenance costs by operating with truly anhydrous electrolyte.

The other high cost component in the production of electrolytic magnesium is the electrolysis operation itself as a consequence of its demand for electricity. All electrowinning processes have this same expense. Indeed, the electrical energy consumption of the major electrometallurgical processes used in the United States and Canada is estimated to be 5 percent of total generated electrical energy(46). Although electrolytic industries, notably in the chloro-alkali sector, have developed ways to save electrical energy, from this study it is apparent that modifications in any of the existing cell designs will have only a modest impact in this regard. Both the Alcan and Norsk Hydro cells in their latest models can boast of cathode current efficiencies in excess of

90 percent. The Dow cell operates at about 80 percent current efficiency; but then, this is offset by savings in dehydration by the use of an electrolyte containing 1.7 moles of water per mole of magnesium chloride.

This is not to say that there is little room for improvement. It is important to make metallurgical processes go as quickly as possible to obtain high outputs from small reactors which generally have lower capital costs. Electrolysis distinguishes itself as having among the lowest rates of processing where such are expressed as mass of metal produced per unit time per unit volume of reactor. For example, the copper converter produces metal at a rate 80 times that at which a Hall cell produces aluminum(47). The bottom-blown oxygen converter produces steel at a rate 140 times that at which copper is electrolytically refined(47). Low processing rates are achieved in operations in which the interfacial area is small and/or transport of reactants to these interfaces is rather slow because of poor circulation. Obviously what is needed in this area is a radically innovative approach to cell design. In large measure the trail has been blazed by electrochemical engineering inventions in aqueous cells.(48) In his review of industrial electrochemical process cell designs Jackson(49) was prompted to write that "for various reasons cells operating with molten salt electrolytes are still little more than giant 'pots'".

Thus, the goal of research in the general area of cell design must be not only to minimize the number of kWh/lb magnesium but to produce the metal at much faster rates than any of the present electrolytic processes. In short, unless electrolytic inventions result in an order of magnitude increase in space/time yield, one can expect potential new producers of magnesium (or even those currently in the business who may be considering expanding production capacity) to avoid electrolysis altogether and to choose from among the various thermochemical technologies.

3.6.2 Recommendations for Future Work

3.6.2.1 Dehydration

From an economic standpoint there is no fully satisfactory commercial dehydration process at present. Its development is essential if electrolytic magnesium production is to remain viable. Fully half the cost of production lies in cell feed preparation. Additionally, regardless of improvements in cell design, the full advantages of electrolysis are never realized as long as impurities are present in the electrolyte. At the moment one is faced with the choice of a number of drying technologies, notably spray drying, flash calcining, fluidized bed processing, reacting in organic solvents, and reacting in molten salts. Each has its advantages. Some produce cell feed of extremely high purity but at an unacceptably slow rate. Others have high yields but at still intolerable impurity levels. Some have never been applied to the problem of dehydration of magnesium chloride for electrolysis cells and, thus, the data base is incomplete. For example, although the data for the magnesium chloride-water equilibria have been reported, the results of some recent spray drying experiments are contradictory. Perhaps this is due to incomplete reaction. But, then, there is little published about the kinetics of dehydration of magnesium chloride. In short, it is difficult to select a "best" technology worth supporting. Accordingly, it is recommended that a two-year research program be conducted to acquire a complete data base to guide the development of a new commercial dehydration technology. Parts of the program would best be performed at the university; others in industry. Certainly, industrial cooperation is foreseen in many of the suggestions.

RECOMMENDATION D1: *Make the necessary thermodynamic and kinetic measurements of the dehydration of hydrated* $MgCl_2$ *to provide a thoroughly adequate data base for the development of dehydration technologies. Of the current commercial inventions, solar evaporation consumes the least energy. A special effort should be made in studying the product of solar ponding. Optimistically, the latter could be eventually treated in one chemical reaction step to produce anhydrous electrolyte.*

The electrolyte ultimately consists of a solution of $MgCl_2$ in one or more alkali-metal and alkaline earth chlorides. In order to reduce the number of processing steps in preparation of the cell electrolyte one could mix the alkali chlorides with hydrated $MgCl_2$ prior to dehydration. In this way the product of dehydration could be charged directly into the electrolysis cell without further handling.

RECOMMENDATION D2: *Investigate the effects of alkali-metal and alkaline-earth chlorides on the dehydration of hydrated* $MgCl_2$.

Should lithium chloride become a primary constituent of the electrolyte as a result of changes in electrochemical cell design, its efficient dehydration would require attention. Unlike sodium and potassium chlorides, lithium chloride has a strong affinity for water and will hydrolyse upon heating.

RECOMMENDATION D3: *Make the necessary thermodynamic and kinetic measurements of the dehydration of hydrated* $LiCl$.

Operation with a lithium chloride based electrolyte would demand removal of not only water but also the heavier alkali-metal chlorides. The latter would enter the cell as minor impurities and accumulate over a period of time. Partial crystallization offers the possibility of reducing the amount of material to be processed (or conversely, the possibility of extending the useful lifetime of a given charge of electrolyte) if the undesirable components prove to be concentrated in the solid phase.

RECOMMENDATION D4: *Investigate the purification of LiCl by partial crystallization by measuring the compositions of the crystals which freeze out of typical lithium chloride based electrolyte melts which have been* contaminated in *a controlled manner.*

Reactor design will be an important factor in determining the final cost of dehydration. The knowledge of the thermodynamics and kinetics of reaction should enable optimal choice in this regard. There are several commercial reactors which can readily be adapted to perform the dehydration of $MgCl_2$ hydrates.

It seems that water removal is not a problem. However, dehydration can be accompanied by hydrolysis. This results in the formation of Mg0 and MgOHCl which cannot be tolerated in the electrolyte. Attention must be given to preventing their formation and/or eliminating them either by chemical treatment or by mechanical means such as sedimentation, filtration, etc.

RECOMMENDATION D5: *Test the dehydration of $MgCl_2$ hydrate both in spray driers and flash calciners to determine lowest contaimination levels of MgO and MgOHCl.*

Chemical treatment to eliminate oxides and oxychlorides typically involves chlorination in the presence of a reductant such as carbon. Bubbling chlorine through a melt of dehydrated $MgCl_2$ containing the impurities offers the advantage of rapid kinetics because the reaction is gas/liquid. However, there is evidence in the literature to recommend that one avoid melting oxygen bearing chloride melts and that one reduce the contaminants in the solid state.

RECOMMENDATION D6: *Determine mass transfer rates for the carbochlorination of MgO in a molten chloride by (i) bubbling chlorine/HCl in the presence of finely divided carbon, (ii) bubbling a gas mixture of CO, HCl and Cl_2, (iii) bubbling phosgene ($COCl_2$).*

RECOMMENDATION D7: *Determine mass transfer rates when solid particles of dehydrated* $MgCl_2$ *containing oxide and oxychloride impurities are chlorinated in a fluidized bed with (i) chlorine/HCl in the presence of finely divided carbon, (ii) a gas mixture of CO, HCl and* Cl_2*, (iii) phosgene and determine the parameters which affect the purity of the product so produced.*

RECOMMENDATION D8: *Determine purity levels which can be achieved by elimination of oxygen bearing insolubles in anhydrous* $MgCl_2$ *by filtration and sedimentation techniques.*

The highest purity anhydrous $MgCl_2$ reported in the literature as having been produced at the commercial level is that made by chemical reaction of the hydrated $MgCl_2$ with an organic reagent which has an extremely high affinity for water.(4) The viability of this operation depends upon one's being able to recycle the hydrated organic reagent.

RECOMMENDATION D9: *Verify the claims of purity of disclosed solvent extraction processes and test their commercial viability by analysis of optimum operating parameters.*

3.6.2.2 Electrolysis

The most important problem to be solved in electrochemical reactor design is that of mass transport enhancement. As the economic section of this report will testify, the use of magnesium in transportation is restricted not by price alone but rather by its limited availability, i.e. a combination of inadequate tonnage and too few suppliers. Because the electrolytes discussed herein must contain magnesium chloride at reduced concentrations for reasons of its volatility, care must be taken to furnish a constant supply of electroactive species to the electrode surfaces. It is clear that better engineering can result in improved space/time yields which are mandatory if electrolysis is to compete with large scale pyrometallurgical processes. Much work has been done in this regard with aqueous electrochemical cells(48). However, this does not mean that one is free to choose from among the more successful designs in order to make magnesium. The properties of molten magnesium chloride - alkali chloride are somewhat different from those of an aqueous electrolyte. And what is more significant, the cathodic product is molten. Preventing the metallic product from chemically reacting with the gas produced at the anode is much more difficult when the metal is fluid. Parenthetically, in a molten salt electrolysis cell producing magnesium and chlorine at 750°C, the volumetric ratio of gas to metal droplet is 5500:1.

What is needed is a comprehensive study of fluid flow patterns in electrolysis cells. This knowledge will provide a data base from which to work on cell designs which exploit the flow of electrolyte to separate the products, Mg and Cl_2. Some proposals have been made in this area.(50)

To reduce capital costs it is necessary to increase cell throughput. This requires maximizing cathode surface area.

RECOMMENDATION E1: *Assess various cell designs by measuring fluid flow patterns of water model representations using cinephotography, hot-wire anemometry, and laser Doppler anemometry. This would be coupled with mathematical modelling of the system along hydrodynamic lines.*

One of the problems facing design engineers is scale-up of laboratory cells to commercial size or even pilot plant size for that matter. There is room for supportive research in the form of detailed comparison of the characteristics of intermediate size molten salt cells with the characteristics of laboratory cells and water models.

RECOMMENDATION E2: *Measure and compare the operating characteristics of intermediate size molten salt cells with those of laboratory cells and water models.*

Despite the high current efficiencies attained by contemporary electrolytic cells, much can still be done to reduce overvoltages and enhance the surface reaction rates at the electrodes.

RECOMMENDATION E3: *Study the electrode kinetics of magnesium reduction in various solvent melts to determine the parameters which may be adjusted to maximize reaction rates with a view to improving ultimate space/time yields. The techniques to be used include emf measurements, linear sweep voltammetry, chronopotentiometry, chronoamperometry, and pulse polarography.*

RECOMMENDATION E4: *Compare the cell performance of vertical monopolar electrodes, vertical and horizontal bipolar electrodes, and porous electrodes.*

RECOMMENDATION E5: *Study the electrode kinetics of chloride oxidation at the anode and subsequent formation of chlorine gas bubbles. Factors affecting anodic overvoltage should be determined as a function of electrode shape, composition, temperature and current density.*

Even in the purest of electrolytes, consumption of the anode accompanies electrolysis. This problem is particularly severe in the case of Dow cells with their partially hydrated electrolyte. Apart from requiring costly interruptions in production in order to install new anodes, their degradation results in a change of shape which changes their electrical "throwing power" in the melt. Another approach to the problem of anode wear is to allow it to occur, but in a predictable way so as not to disturb the electrolysis.

RECOMMENDATION E6: *Search for new materials which can serve as dimensionally stable anodes.*

In the electrodeposition of solid metal the literature tells of the benefits of deviating from electrolysis driven by a constant d.c. voltage. The results pertain mainly to the improvement of the morphology of the solid electrodeposit. It is unknown whether such electrical variations would be beneficial in the case of a molten electrodeposit.

RECOMMENDATION E7: *Investigate the effects of periodic reversal of electrode polarity and superposition of an a.c. voltage on the d.c. decomposition voltage. A molten salt test cell using several candidate electrode designs would be employed. Obviously one expects no variation in morphology; however, there may be some enhancement in mass transfer rates at the electrode surface caused by the disruption of the melt boundary layer.*

Mechanical forms of agitation are also worth considering in attempting to improve mass transfer of the electroactive species and also to prevent the chemical recombination of magnesium and chlorine in the cell.

RECOMMENDATION E8: *Test the effects of forced circulation of the electrolyte and ultrasonic agitation of the electrodes. This would be performed on several prototype electrode designs in a laboratory cell.*

3.7 REFERENCES

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4. TECHNOLOGY ASSESSMENT OF THERMIC MAGNESIUM PRODUCTION AND RECOMMENDATIONS FOR RESEARCH AND DEVELOPMENT

4.1 INTRODUCTION

The first thermic magnesium production plants in the United States were built during the Second World War when the demand for magnesium increased rapidly(1). By the end of 1945, with the loss of wartime demand for magnesium, only Dow Chemical with its seawater, electrolytic process remained as a domestic producer(2,3). Except for a short period during the Korean conflict, thermic production was not a significant factor in the United States until 1976 when Northwest Alloys, a subsidiary of Alcoa began magnesium production in Addy, Washington using SOFREM's Magnetherm process.

The majority of the world supply of primary magnesium is produced by the electrolysis of fused magnesium chloride. However, as illustrated in Table 4.1.1, thermic production facilities, representing approximately 28 percent of current Western World production capacity, outnumber the electrolytic facilities. This is attributable to the simplicity of thermic reduction equipment design and ease of operation. Thermic facilities also have the advantages of less restrictive site selection criteria, low capacity economies of scale, and consequently lower initial investment requirements. These factors are reflected in the selection of thermic processes by producers in Brazil, Canada, France, Italy, Japan, and Yugoslavia, where only limited domestic markets for magnesium currently exist(4).

Until the recent development by Norsk Hydro of a new electrolytic process which is expected to be economical at 20,000 tons/year, the minimum scale for an independent electrolytic facility was considered to be greater than 30,000 tons/year. This economy of scale factor for thermic and electrolytic facilities is reflected in the rated annual capacities of the

TABLE 4.1.1

World Magnesium Production Capacity

	Company	Process	Annual Capacity (tons)
Brazil[+]	Brasiliero de Magnesio	Magnethermic	6,000
Canada	Chromasco Limited	Silicothermic	11,000
France	Societe Francaise d'Electrometallurgie (SOFREM)	Magnetherm	9,900
Italy	Societe Italiana per il Magnesio e Leghe di Magnesio	Silicothermic	12,700
Japan	Furukawa Magnesium, Ltd.	Silicothermic	7,200
	Ube Industries, Ltd.	Silicothermic	7,200
Norway	Norsk Hydro	Electrolytic	55,000
U.S.S.R.	Various	Electrolytic	(71,000)*
United States	Dow Chemical Company	Electrolytic	125,000
	NL Industries	Electrolytic	28,000
	Northwest Alloys (Alcoa Subsidiary)	Magnetherm	24,000
	American Magnesium Company	Electrolytic	10,000
Yugoslavia	Magnohrom Oour Bela Stena	Magnetherm	5,000
		TOTAL	301,500

[+] Expected to begin production in 1982.

*Estimate not included in total.

Sources: U.S. Bureau of Mines Minerals Yearbook, Canadian Department of Energy, Mines and Resources, International Magnesium Association, and Personal Communication.

facilities listed in Table 4.1.1. American Magnesium, the only electrolytic exception, had originally planned to expand its start-up capacity of 10,000 tons to 30,000 tons/year. These plans were reiterated in 1977, however, there has been no confirmation of this.

Metallothermic production of magnesium is based on the reduction of magnesium oxide with an acceptable reductant, under suitable conditions of temperature and pressure. For the present analysis of current and potential metallothermic methods of magnesium production, the overall process shall be divided into three major process components as in Figure 4.1.1.

Raw material sources for magnesium production are essentially unlimited within the United States. These include seawater, brines, bitterns, wash liquors from potash and soda facilities, and common oxide, carbonate, chloride, and silicate materials. How these raw materials are converted to thermal reduction unit feed will be treated in a later section.

The principal reductants in thermic processes are calcium, aluminum, silicon, and carbon. These reductants can either be used as pure elements or as compounds or alloys including calcium carbide, calcium silicide, aluminum silicon, scrap aluminum, and ferrosilicon.

The choice of reductant is a major factor in the determination of the optimum operation of the metallothermic process. The reductant, together with the magnesium feed material and required additives, determine the slag melting temperature and subsequent minimum operating temperature, and ultimately the magnesium metal production rate(5). These and other factors will be discussed in detail as they apply to each thermic process.

The thermal reduction unit supplies the heat required to drive the reaction which produces a molten slag and magnesium vapor. The predominant thermic processes in use today operate so as to produce a magnesium-bearing

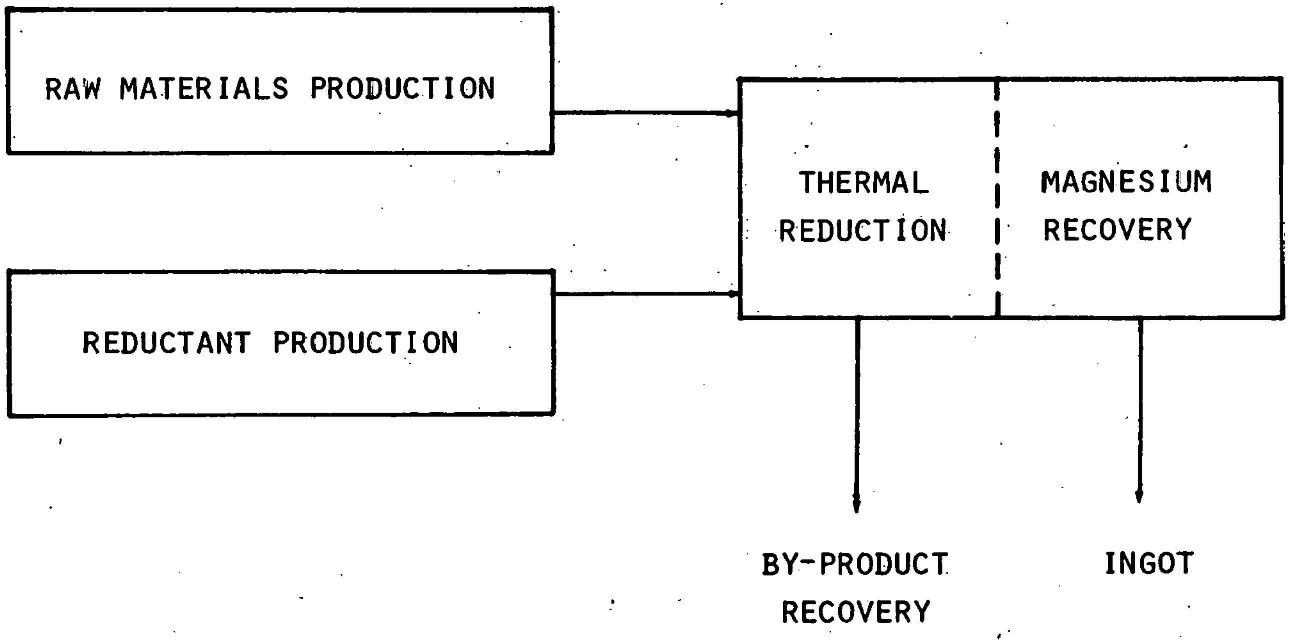

Figure 4.1.1: Metallothermic Process Outline.

vapor phase. This can be accomplished using reductants such as calcium, aluminum, silicon, or any combination thereof. These materials reduce magnesium oxide by producing nonvolatile oxides of their own, plus magnesium vapor. If carbon is used as the reductant, magnesium vapor and carbon monoxide gas are produced.

The equilibrium partial pressure of the magnesium vapor is a function of the operating temperature of the thermal reduction unit. As temperature increases, the driving force for chemical reduction increases and results in an increased equilibrium partial pressure of magnesium vapor. It is the combination of the reductant with its corresponding magnesium vapor pressure versus operating temperature profile which determines the optimum operating conditions and design of the thermal reduction unit. The only technical constraint on the maximum operating temperature (and corresponding magnesium production rate) is the limitation of the materials of construction available to contain the reaction.

Owing to the limitation of materials to contain the thermic reactants at high temperatures and operational problems such as slag carryover to the condenser at excessive temperatures, it has been necessary to carry out the reduction reactions at temperatures between 1500°C and 1700°C. Within this temperature range the reaction will proceed at a reasonable rate with the reductants calcium, silicon, or aluminum, all of which produce nonvolatile oxides. Even though the resulting vapor pressure of magnesium may be only a fraction of one atmosphere under these conditions, it still greatly exceeds that of the other components of the reaction. The magnesium vapor produced in the furnace is induced to leave the reaction zone and to enter the condenser for collection by distillation. This may be accomplished with the aid of a sweeping gas or by diffusion promoted by the evacuation of the vessel containing the reaction. The success of such a reduction operation depends critically upon maintaining a very low magnesium vapor pressure above the reactants in the furnace since it is the difference between the magnesium vapor pressure above the melt and the equilibrium partial pressure of magnesium at the surface of the melt which determines the reaction rate. This reduction procedure, which is applicable only to reductants which produce nonvolatile oxides, is considered under the general classification of metallothermic processes(5).

The thermal reduction of magnesium with carbon, referred to as the carbothermic process, has been successfully demonstrated on an industrial scale but is not currently in service anywhere in the world(6). With this process, carbon monoxide is co-produced with the magnesium vapor. Since the reverse reaction of magnesium oxidation by the carbon monoxide gas occurs in the temperature range between 1850°C and 450°C, the simple distillation procedure used in metallothermic processes for magnesium collection cannot be used. To avoid reoxidation of the magnesium vapor product, the carbothermic process is conducted above 1850°C and the magnesium vapor is collected by shock-cooling the product gases rapidly through the unstable 1850°C to 450°C range. This process and subsequent modifications are discussed in a later section of this report.

4.2 CURRENT AND ONGOING RESEARCH AND DEVELOPMENT

By the end of World War II, all the metallothermic and carbothermic magnesium facilities in the United States were closed in favor of the more efficient electrolytic process. The Pidgeon silicothermic process did survive in other countries and was reintroduced into the United States for a short period during the 1950's and 1960's. Currently, the only thermic magnesium operation in the United States is that of Alcoa's Northwest Alloys facility which began production in 1976. All existing thermic facilities are listed in Table 4.1.1.

Current and ongoing research by the major thermic producers and other groups are reviewed as follows:

CHROMASCO LIMITED, Haley, Ontario

Magnesium has been produced in Canada since the early 1940's using the Pidgeon process. Chromasco is currently the only magnesium producer in Canada and has made many improvements in the Pidgeon process(7). One specific improvement has been the mechanization of the retort charging and discharging operation. This development has reduced the labor requirement and also improved the efficiency of the process. Efforts are continuing in the area of process automation and computer control.

SOCIETE FRANCAISE d'ELECTROMETALLURGIE (SOFREM), Marignac, France

The Magnetherm process began commercial operation in France in 1964. It is currently being operated under license in the United States by Alcoa, and by Magnohrom in Yugoslavia. An excellent account of the reaction mechanism and equilibria of the Magnetherm process has recently been published(8).

The initial Magnetherm furnace was a 2,000 kW unit with a production capacity of 2.5 tons per day. The current furnace operates at 4,500 kW and produces 7.5 tons of magnesium daily. Efforts are underway to replace the existing single-phase power supply with a three-phase system. The three-phase furnace would have a power rating of 10,000 kW and a potential production capacity of 10 to 12 tons per day. The problems with such a development are the out of balance loading of the three electrodes which leads to (1) irregularities in the formation of the solid slag layer which lines the surface of the furnace wall, and (2) problems with solidification of the slag at the bottom of the furnace.

Improvements in the Magnetherm process over the last five years have been substantial(9). These include computer monitoring and control of furnace operations, modification of the vacuum and condenser system, and the development of a new slag tap plugging machine. The result has been a 45 percent increase in the daily production rate of the furnace, a substantial decrease in raw material, energy, and labor requirements, plus a 13 percent increase in the magnesium recovery ratio. Continuing research efforts are being directed towards further improvements in condenser design and efficiency which continues to constrain furnace production capacity. A method is also being developed to permit slag removal without breaking the vacuum of the system.

DOW CHEMICAL COMPANY, Midland, Michigan

Dow has recently been granted a U.S. Patent covering the chemicothermal production of magnesium(10). A two-stage process is described wherein magnesium metal is produced by metallothermic reduction of magnesium oxide using an aluminum alloy. The alumina slag produced by the metallothermic reduction of the magnesium oxide is bled from the furnace to an adjacent carbothermic reduction unit where the aluminum alloy is regenerated. This alloy is then recirculated to the metallothermic reduction unit for reuse.

REYNOLDS METALS COMPANY, Richmond, Virginia

Reynolds has been granted a U.S. Patent covering the metallothermic production of magnesium using an aluminum silicon alloy as the reductant(11). Magnesium oxide is fed in less than stoichiometric amounts which means that not all of the aluminum is consumed and a pool of aluminum silicon alloy forms in the bottom of the furnace. This alloy is recovered and may be used in the production of silicon alloy products. The advantages of this system are that magnesium vapor is produced at atmospheric pressure and the metal is collected as a liquid. These are the conditions necessary for conversion of the metallothermic process to continuous operation. Unfortunately, this process may be economically constrained by the price of aluminum silicon reductant.

SHOWA DENKO K.K., Tokyo, Japan

Showa Denko has in the past operated a small metallothermic magnesium facility. Several U.S. Patents have recently been granted to Showa Denko which describe a novel metallothermic process based on the use of a silicon calcium alloy reductant(12,13). The silicon calcium alloy is produced in a preliminary stage by roasting briquets of silicon, ferrosilicon, and dolime in an inert atmosphere at a temperature above the melting point of the alloy. The magnesium oxide reduction reaction is suppressed at this stage. The briquets are subsequently heated thereby reducing the magnesium oxide component.

PARLEE-ANDERSON, Urbana, Illinois

In 1974, Professors N. Parlee* and R. Anderson* were granted a U.S. Patent covering a new carbothermic reduction method for converting oxides of reactive metals to metallic form. The Parlee-Anderson process is based on utilization of the unique properties of liquid metal solvents which tend to drive the reduction reaction to the right at reduced operating temperatures by lowering the activity of the magnesium metal. Since the magnesium is retained in the solvent metal, the back

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* Department of Applied Earth Sciences, Stanford University, Stanford, California 94305.

reaction of magnesium with the carbon monoxide is avoided(14-16).

Much of the ongoing research and development work to adapt the Parlee-Anderson process to magnesium metal production is being directed by Professor C. Eckert**. Extensive investigations have been made of the thermodynamics of magnesium solvent metal systems and both experimental and theoretical models have been developed. This research and development effort is continuing. Much of the past data and recent conclusions are well documented as advanced degree theses completed under Professor Eckert's direction(17-21).

BILLITON RESEARCH B.V., Arnhem, Netherlands

While attending the International Conference on Magnesium held at Massachusetts Institute of Technology, Cambridge, Ma., in 1977, a representative of Billiton International Metals B.V. announced an ongoing research program directed towards the development of an improved carbothermic process. At that time the research effort was centered on the magnesium vapor collection problem of avoiding the back reaction between carbon monoxide gas and magnesium vapor on quenching.

Billiton researchers have found that the carbothermic magnesium reduction reaction can be carried out at tmeperatures as low as 1000°C, if iron, cobalt, nickel, chromium, or manganese is also present in the reaction mixture(22). The function of the metal component is not entirely clear. However, it has been found that the reverse reaction of the magnesium vapor and carbon monoxide gas is suppressed. Collected in a simple water-cooled condenser, the magnesium metal product has a purity in excess of 95 percent.

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TOYO SODA MANUFACTURING COMPANY, Tamaguchi, Japan

Toyo Soda has developed an apparatus for the carbothermic reduction of magnesium oxide(23). This apparatus is based on the use of a high velocity, inert, sweeping gas. The gas jet is directed across the top of the furnace and through an outlet port to a metal collecting unit. This gas jet acts to transport the magnesium vapor from the furnace while simultaneously acting as a quenching medium. The recovered product is 85 percent magnesium by weight.

CARBOTHERMIC, Hyoken, Japan

Mr. F. Hori of Japan has recently been granted a U.S. Patent covering a novel apparatus for the collection of magnesium produced carbothermically(24). With this apparatus, the magnesium vapor and carbon monoxide gas are held above the recombination temperature until effectively separated for collection. The two components are separated as the total gas mixture is accelerated through a divergent nozzle under conditions of underexpansion. Since the two gases have different values of specific heat, they diverge at different angles at the nozzle exit and separate from each other. The gases leave the nozzle at supersonic speeds and are thereby rapidly separated and quenched to provide a magnesium product of high purity.

UNIVERSITY OF SHERBROOKE, Montreal, Canada

In 1977, a researcher at the University of Sherbrooke reported the discovery of a process for extracting magnesium from asbestos waste. Plans have been announced to build two pilot plants to be known as Magnaq One and Two at Thetford Mines, Quebec. These facilities are expected to produce 11,000 tons of magnesium annually, plus either 5,000 tons of magnesium oxide or 10,000 tons of magnesium carbonate.

In order to delineate the areas of probable greatest payoff in terms of operating costs and energy savings, a detailed technical analysis of existing proposed, and developing thermic processes is presented in the three following subsections.

4.3 Raw Materials

While magnesium does not occur elementally in nature, it is found in more than 150 minerals. The principal raw materials for thermic magnesium processes with their chemical compositions and magnesium oxide and magnesium contents are listed in Table 4.3.1. Magnesium salts, as obtained from seawater, bitterns, and well brines, are also included as potential sources of magnesium oxide. The global reserves of magnesium raw materials are well documented and essentially inexhaustible(25,26).

Of the raw materials listed in Table 4.3.1, magnesium is currently produced thermically from dolomite and magnesite. Other attractive sources include olivine, serpentine, and magnesium chloride contained in sea water, well and lake brines, and wastes of the potash and soda industries. Magnesite, dolomite, and magnesium chloride brines are the only materials to date which have been used commercially as magnesium raw materials in thermic processes.

4.3.1 Availability

Periclase and brucite are the richest naturally occurring magnesium compounds. However, these are not acceptable raw materials because they are, in general, widely distributed in unworkably small amounts. The largest known commercial deposit of brucite, estimated at 3,000,000 tons, is located in Nevada. This deposit, found adjacent to magnesite and dolomite, is also

TABLE 4.3.1

Principal Magnesium Raw Materials

		Composition	MgO Percent	Mg Percent
Oxides	Periclase	MgO	100.0	60.3
	Brucite	$Mg(OH)_2$ or $MgO \cdot H_2O$	69.1	41.7
Carbonates	Magnesite	$MgCO_3$	47.8	28.8
	Dolomite	$MgCO_3 \cdot CaCO_3$	21.8	13.2
Silicates	Olivine	$(Mg,Fe)_2SiO_4$	55.0	27.0
	Serpentine	$3MgO \cdot 2SiO_2 \cdot 2H_2O$	43.6	26.3
	Enstatite	$MgSiO_3$	40.0	24.0
Sulfate	Keiserite	$MgSO_4 \cdot H_2O$	29.2	17.6
Chlorides	Bischoffite	$MgCl_2 \cdot 6H_2O$	19.9	12.0
	Carnallite	$MgCl_2 \cdot KCl \cdot 6H_2O$	17.8	8.8
	Brines	$(Mg,Ca,K,Na)X_n$ where $X = Cl_2, SO_4, \ldots$		>1.0
	Sea Water	MgX_n where $X=Cl_2,SO_4,\ldots$		0.14

irregular in shape and distribution.

Magnesite and dolomite occur in considerable deposits in various parts of the United States and the world. Magnesite occurs principally in California, New Mexico, Texas, Nevada, and Washington where reserves in excess of 7 million tons have been estimated in one county alone. Enormous quantities of high-grade dolomite deposits, each having reserves in excess of a million tons, exist in at least a dozen states from coast to coast.

The largest deposits of olivine are located in Washington, North Carolina, and Georgia where it exists as dunite, a rock consisting almost entirely of the mineral olivine. Locally, some of these deposits are altered to serpentine and talc. Twenty of the largest and most readily accessible North Carolina-Georgia deposits contain an estimated 230 million tons of unaltered olivine, averaging 48 percent magnesia. However, the Twin Sisters Mountain area of Washington, with reserves estimated in the millions of tons, represents the largest deposits of fresh olivine within the United States.

The single largest potential source of magnesium oxide is hydrated magnesium chloride as found in the sea water, salt lakes, and industrial by-product streams. As such, these represent an essentially infinite reserve of magnesium.

4.3.2 Raw Material Feed Preparation

The preparation of magnesium-containing ores for use as reduction cell feed material is a minor component of the overall operation and cost of thermic magnesium processes. This is one of the principal advantages of thermic production methods. For this reason, only magnesium oxide produced from magnesite, dolomite, and hydrous magnesium chloride will be considered here.

A. Magnesite and Dolomite

Most of the potential starting materials for thermic production of magnesium must undergo a preliminary heat treatment to dissociate and remove volatile components. If not removed, these volatile components would disrupt the reduction process by contaminating the magnesium vapor produced. Thus, magnesite and dolomite are calcined to decompose the carbonates as follows:

$$MgCO_3 \rightarrow MgO + CO_2(g)$$

$$MgCO_3 \cdot CaCO_3 \rightarrow MgO \cdot CaO + 2CO_2(g)$$

The rate of calcination is controlled primarily by the supply of the necessary heat of decomposition by conduction through the outer layer of burned material. Consequently, the rate of calcination is diffusion controlled and is proportional to the square of the diameter of the raw material particles. While the calcination rate can be accelerated with higher operating temperatures, this may result in overheated products and subsequent loss of chemical reactivity. The calcination temperature also affects grinding, susceptibility to hydration and carbon dioxide absorption, density, and possibly the content of alkali elements in the magnesium oxide product.

For industrial applications, calcination may be carried out in a shaft furnace, rotary kiln, or fluidized bed(27). The choice of the apparatus and temperature to be used is determined by the desired properties of the calcined product.

B. Magnesium Salts

If magnesium oxide is to be produced from magnesium chloride salts, two basic processes are available. In one case the magnesium is retrieved as a hydroxide which is directly calcined to magnesium oxide. In the other process, hydrous magnesium chloride liquor is dried and calcined in stages to produce high purity magnesium oxide plus hydrochloric acid.

To recover magnesium as magnesium hydroxide, sea water, well or lake brine, or by-product magnesium chloride liquor is treated with either lime or dolime. The basic reactions are as follows:

$$CaO + H_2O \rightarrow Ca(OH)_2$$

or

$$MgO \cdot CaO + 2H_2O \rightarrow Ca(OH)_2 + Mg(OH)_2$$

and

$$Ca(OH)_2 + MgCl_2 \rightarrow CaCl_2 + Mg(OH)_2$$

If dolime is used to precipitate magnesium hydroxide from a magnesium chloride containing solution, the magnesium content of the dolime is recovered with that of the brine, in equal proportions.

The precipitated magnesium hydroxide slurry, recovered from thickeners, is filtered to produce a magnesium hydroxide cake containing approximately 50 percent water. This cake is calcined in a rotary kiln to produce magnesia of 97 percent purity.

The total energy requirement for this type of operation, using dolomite and sea water, has been estimated at 18.6 million BTU/ton of magnesia produced(6).

In the hydrous magnesium chloride liquor process, the optimum raw materials are either potash and soda industry waste liquor or solar evaporated brines. In both cases the starting material contains approximately 26 percent magnesium chloride, plus relatively high concentrations of other impurities. These impurities, particularly potassium and sodium chlorides, are removed from the liquor as precipitates. The order and degree of precipitation can be determined from solubility curves where the solubility of the extraneous salts decreases sharply with increasing magnesium chloride concentration. At a magnesium chloride concentration of approximately 32 percent, the clarified liquor is ready for final processing to magnesia and hydrochloric acid. This process is also described in detail in the literature and is only outlined here(25).

The clarified liquor is dried to nearly two moles of water before being charged into a rotary kiln where it is calcined to magnesium oxide by the following reaction:

$$MgCl_2 \cdot 2H_2O = MgO + 2HCl + H_2O$$

The product is of very high purity, consisting of approximately 99.8 percent magnesia. The hydrochloric acid can be conveniently collected as 20 percent acid and can be sold as a by-product.

Since the raw materials for magnesia production are readily and economically available as either minerals or salts, raw materials availability as one of the potentially constraining factors with respect to site selection is minimized. This permits the optimization of the remaining combination of geographic and economic factors such as reductant and energy sources, plus by-product markets.

4.4 REDUCTANTS

The choice of the reductant to be used is a major factor in the determination of the operating cost and energy efficiency of thermic magnesium primary production processes. However, the choice of the reductant has only minimal effect on the basic design of the typical metallothermic reduction facility. Therefore, a comparison of the merits of the various reductants can be made while assuming that the choice of the optimum reductant can be made independently of basic metallothermic facility design considerations.

The principal reductants to be considered include elemental and alloyed calcium, aluminum, and silicon. Carbon is included as part of this comparative analysis but it should be recognized that the metallothermic and carbothermic processes embody fundamental design and operating differences. Most research and development efforts have been directed at the four reductants listed.

In 1965, the Bureau of Mines presented a detailed analysis of the metallothermic process. Included was a comparative evaluation of potential reductants(5). A modified and updated review of this reductant appraisal is presented to reflect current technical and economic conditions. This review of the effects of the choice of reductant on the operating cost and energy efficiency of thermic magnesium production processes is based on the following factors:

1. The electrical energy requirement for the production of the reductant: This factor is reported per ton of reductant and per weight of reductant theoretically required to produce one pound of magnesium. A measurement of the overall energy efficiency of the magnesium thermic processes must include not only direct process energy requirements but also the energy content of all input materials not produced in-house.
2. The reductant market price: This factor, combined with the theoretical amount of reductant required to produce one pound of magnesium, establishes a basis for comparing this operating cost component.

3. The equilibrium partial pressure of magnesium versus temperature: The rate of magnesium production in the furnace at a given temperature is determined, among other things, by the rate of gaseous magnesium evolution and the speed with which this product is removed from the reaction zone. The driving force for removal of the magnesium vapor from the reaction zone is the pressure differential between the furnace and condenser. Therefore, for a given magnesium vapor pressure at the condenser surface, the overall magnesium production rate will be a function of the equilibrium partial pressure of magnesium for the reduction reaction.
4. The theoretical volume of the charge per pound of magnesium produced: For a given size reduction cell, the production of magnesium per cycle (in a batch operation) varies inversely with this factor.

The reductants to be considered on the basis of these factors are listed in Table 4.4.1 with the corresponding calculated and experimentally measured equilibrium partial pressures of magnesium presented in Figure 4.4.1. Except for the calcium carbide reaction, the experimentally measured vapor pressures are roughly 5 to 8 times larger than the calculated values(5). The disagreement in these values is somewhat greater than expected from such thermodynamic calculations and may be explained in two ways. First, the stated reaction equations may be oversimplifications of the actual reactions. Secondly, the calculated values are based on inadequate thermodynamic data. Figure 4.4.1 presents a plot of the temperature dependence of magnesium vapor pressure. The calculated magnesium partial pressures are, except for calcium carbide, not in good agreement with the experimental values.

TABLE 4.4.1

Factors of Comparison for Selected Reductants

	Reaction/Reductant	Kwh per ton	Kwh per lb. Mg	Cost per ton	Weight of Reductant, lbs. per lb. Mg	Cost of Reductant, cents per lb. Mg	Volume of Charge, cu. ft. per lb. Mg	Cycle time hrs.
1.	Aluminum (98% Al) $3MgO + 2Al \rightarrow Al_2O_3 + 3Mg$	23,250	8.72	1,520	0.75	57.0	0.0118	4
2.	Aluminum (98% Al) (Scrap)	23,250	8.72	960	0.75	36.0	0.0179	4
3.	Ferrosilicon (75% Si) $2MgO + 2CaO + Si \rightarrow Ca_2SiO_4 + 2Mg$	8,500	3.27	925	0.77	35.6	0.0227	8
4.	Silicon (98% Si) $4MgO + Si \rightarrow Mg_2SiO_4 + 2Mg$	12,000	3.54	1,190	0.59	35.1	0.0223	8
5.	Calcium Carbide (80% CaC_2) $MgO + CaC_2 \rightarrow CaO + 2C + Mg$	3,000	4.935	317	3.29	52.1	0.0300	2
6.	Aluminum-Silicon (40% Al-40% Si) $21MgO + 17CaO + 6Al + 6Si \rightarrow 6Ca_2SiO_4 + 5CaO + 3Al_2O_3 + 21Mg$	10,000	3.95	2,000	0.79	79.0	0.0210	2
7.	Calcium Silicide (20% Ca, 60% Si) $7MgO + 5CaO + Ca + 3Si \rightarrow 3Ca_2SiO_4 + 7Mg$	12,800	5.18	1,420	0.81	57.5	0.0214	2
8.	Carbon $MgO + C \rightarrow CO + Mg$	3,000	0.92	133	0.61	0.61	0.0051	72

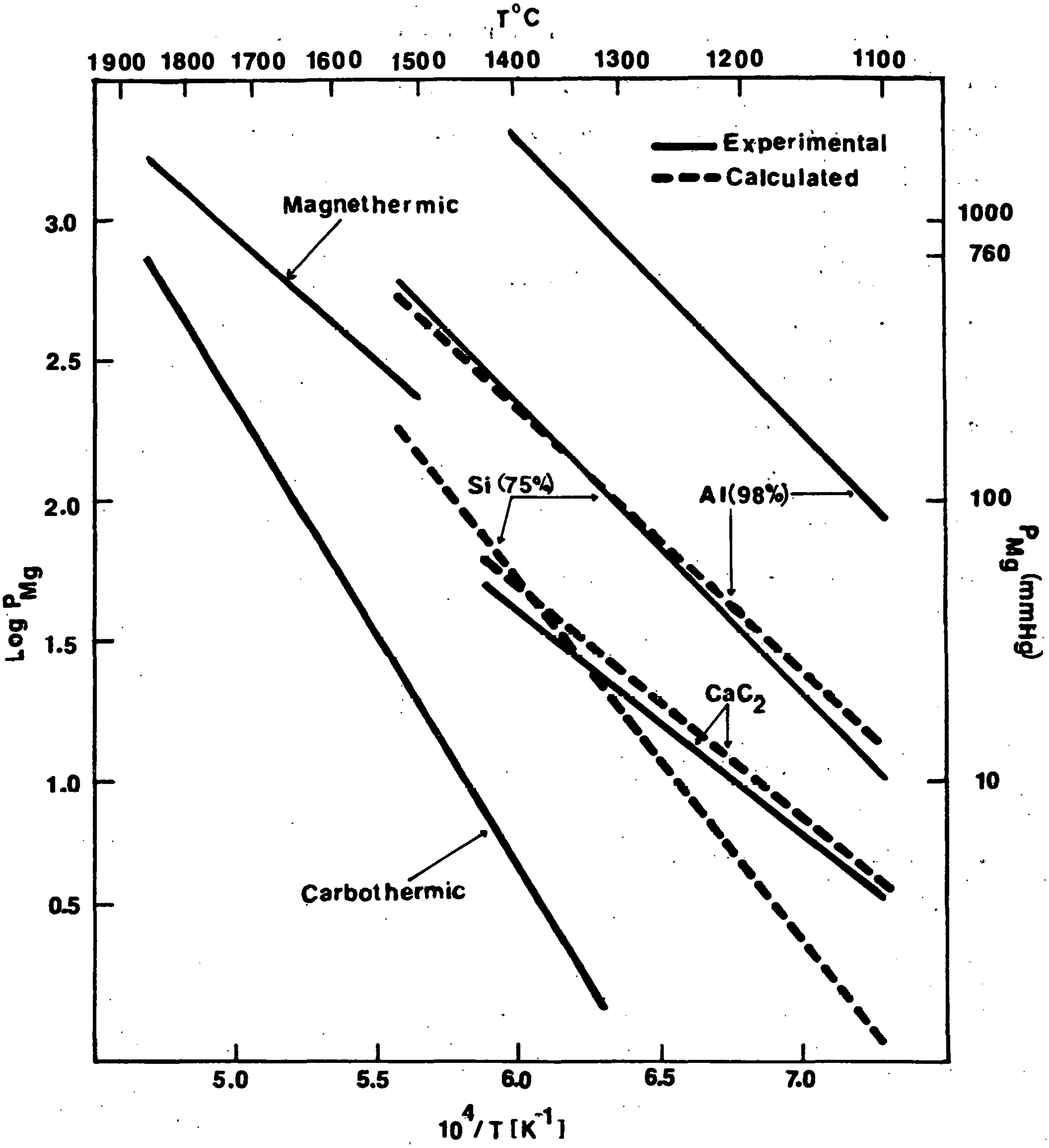

Figure 4.4.1: Experimental and Calculated Values of Magnesium Equilibrium Vapor Pressure Versus Temperature.

Not all the processes and reactions to be discussed in subsequent sections are presented in Table 4.4.1 or Figure 4.4.1 because of the lack of data. However, all the reductant species are represented in Figure 4.1.1, which can be used qualitatively to compare their respective reducing potentials.

It should be noted that the calculated and experimentally measured magnesium partial pressure curves for silicon, below 1400°C, in Figure 4.4.1 refer to the solid-solid phase silicothermic reaction. The molten slag reaction of the Magnetherm process is presented in Figure 4.4.1 for temperatures above 1400°C.

A comparison of the reductants, based on specific input and cost factors, is presented in Table 4.4.1. The data presented in Table 4.4.1 are discussed (in the following subsections) as they apply to the individual reductants.

4.4.1 Aluminum

As indicated in Figure 4.4.1, of all the reductants considered, reaction with aluminum produces the highest calculated and experimentally determined equilibrium partial pressures of magnesium vapor over the temperature range of interest. This factor combined with a low weight and volume of charge per pound of magnesium produced favors aluminothermic reduction as the preferred metallothermic process. However, the cost and electrical energy requirements of primary aluminum production are major deterrents to its use. The use of scrap aluminum does not eliminate the cost constraint because of its price and supply volatility.

Aluminum-silicon alloy has been recommended as a solution to the cost and electrical energy problems associated with the use of 98 percent primary or secondary aluminum. This alloy of 40 percent each of aluminum and silicon represents a compromise between elemental aluminum and silicon. It reduces the electrical energy requirements while producing magnesium vapor pressures intermediate to those of the silicon and aluminum systems.

With respect to price, Table 4.4.1 indicates that aluminum-silicon alloy is not cost effective. However, a 1945 Tennessee Valley Authority report suggests that aluminum-silicon alloys could be produced at a cost comparable to that of ferrosilicon(28). The proposed aluminum-silicon production process involves the electric smelting of various domestically available raw materials, which include kaolin clay and anorthosite, using carbon as the reductant. Alcoa is currently developing a carbothermic smelting process for the production of silicon-aluminum alloy. If successful, it may provide an ideal reducing agent for metallothermic magnesium production. However, at this time it is difficult to project with certainty regarding the availability of aluminum-silicon alloy from this source.

No distinct technical disadvantage can be identified with the use of aluminum-silicon as a thermic reductant. This factor, combined with its potential cost competitiveness and reduced cycle time, suggests that aluminum-silicon is an attractive reductant compared with ferrosilicon.

Municipal refuse incineration plants have also been suggested as a potential source of low grade aluminum alloys. Unless these alloys can be refined and purified, which currently appears to be an expensive proposition, they will continue to be of minimal market value. This low grade aluminum alloy could possibly be used as a metallothermic reductant. The technical feasibility of using low grade aluminum alloys will depend upon the impurities present, the ability to remove some of these prior to use, and the ability of the metallothermic process slag to accommodate and isolate the remaining impurities from the magnesium vapor product stream.

4.4.2 Silicon

The choice of ferrosilicon containing 75 percent silicon as the historically preferred reductant over 98 percent silicon is a function of ferrosilicon production economics. As the content of silicon in ferrosilicon alloy increases, the cost of producing the alloy in electric furnaces increases disproportionately because of higher energy consumption and silicon losses by fuming. Thus, 75 percent ferrosilicon alloy has emerged as the preferred reductant, balancing ferrosilicon production costs against handling and heating costs associated with the diluent iron which does not enter into the metallothermic reduction reaction.

The principal factor favoring silicothermic reduction is the comparatively low cost of the ferrosilicon reductant. The major disadvantages of this procedure are its high charge volume, low magnesium vapor pressure, and extensive cycle time.

Ferrosilicon was the reductant chosen by the most recently commercialized thermic process, the Magnetherm process. This process, versus the solid phase silicothermic Pidgeon process represented by Reaction 3 of Table 4.4.1, normally operates at approximately 1550°C where the reduction reaction proceeds in a molten slag. The Magnetherm process enjoys those operating advantages characteristic of liquid phase, semi-continuous processes. However, it also has a large volume of charge and retains the extensive cycle time disadvantage.

4.4.3 Calcium

Calcium is the thermodynamically preferred reductant. Its oxide has a greater negative standard free energy of formation than magnesium oxide, even at 25°C. However, the use of elemental calcium is economically prohibitive with the market value of calcium exceeding that of magnesium.

Calcium carbide and silicide alloys have been considered as possible alternatives to the use of elemental calcium. Calcium carbide reflects the reducing potential of elemental calcium with a favorable calculated magnesium partial pressure. It also enjoys the advantages of a low reduction cycle time and low reductant production energy requirement. However, these advantages are offset by excessive calcium carbide consumption requirements which are more than 4 times that of ferrosilicon per unit of magnesium produced. This factor generates the subsequent additional disadvantages of high charge volume and weight, plus excessive reductant cost.

Calcium silicide also has the advantage of producing relatively high calculated magnesium vapor pressures. However, calcium silicide, produced by electric furnace smelting of silica with calcium carbide and carbon, is more energy intensive and difficult to produce than ferrosilicon. No real operating data are available for the calcium silicide reduction system and no significant calculated operating or economic advantage can be assigned to it.

4.4.4 Carbon

Based on Table 4.4.1, the carbothermic process for the reduction of magnesium oxide appears to be very attractive, possessing the advantages of the lowest reductant production energy requirements, the lowest cost, and the lowest weight of charge. However, the 72 hour total cycle time experienced in earlier operating plants negates the otherwise competitive position of the carbothermic process.

The technical constraint concerning the recovery of metallic magnesium after successful reduction by the carbothermic process is due to the co-generation of carbon monoxide gas, versus a nonvolatile oxide, in conjunction with the magnesium vapor. Conventional condenser technology for metallic vapor collection cannot be used because the reverse reaction, magnesium oxidation by the carbon monoxide gas, consumes the metallic magnesium if the two components remain in contact between the temperatures of 1850°C and 450°C. The back reaction can be minimized by conducting the reduction reaction above 1850°C followed by a rapid quench of the product gas through the temperature range of product instability. The quenched product of previous commercial facilities typically consisted of dust containing roughly 53 percent magnesium metal, 20 percent unreduced magnesium oxide, 20 percent carbon, and 7 percent other impurities. It is the recovery of the magnesium metal from the dust by sublimation in retorts at 800°C for 48 hours which creates the extensive cycle time experienced in earlier carbothermic production systems.

The conventional magnesium recovery process of the carbothermic process represents as much as 50 percent of the capital and annual operating costs. Thus, while carbon is an ideal reductant, magnesium recovery constrains its utility. The carbothermic process and potential innovations designed to eliminate this constraint will be discussed in detail in a subsequent section.

4.4.5 Other Reductants

Several other materials have been recommended as possible reductants for various magnesium compounds with some of these possibilities representing novel approaches to the simultaneous production of pure magnesium and alloyed metallic by-products(5). For example, ternary alloys of iron and silicon plus manganese, chromium, or nickel have been proposed as possible reductants of dolime or magnesia(29). Operating above the melting temperatures of the ternary ferroalloy, the silicon component of the alloy reduces the magnesium oxide component producing a silicate slag beneath which the binary ferroalloy is obtained. Such co-production of products is not only energy efficient but can also be financially rewarding.

The above process and others not listed here appear to have merit and should not be overlooked as potential alternatives to current technology.

4.5 THERMAL REDUCTION UNITS: EXISTING AND PROPOSED PROCESSES

One of the first methods for producing magnesium by thermic reduction was proposed in 1917 and suggested that magnesium oxide could be reduced with silicon using hydrogen at normal pressures as a gas sweep for collection of magnesium vapor(30). By 1921, thermic processes using calcium carbide and aluminum as reductants of magnesium oxide, plus silicon with dolime as the feed material had been patented(31,32). By 1934, the ferrosilicon reduction process was being used on a small commercial scale in Germany(33,34).

By the end of World War II, all the reductants - calcium, aluminum, silicon, and carbon - had been used in various commercial thermic processes. However, all the thermic facilities in the United States were forced to close by the end of 1945 by the more efficient electrolytic process used by Dow Chemical Company. During the Korean conflict, four of the more efficient silicothermic facilities built in the United States during World War II were reopened by the government, with three of these being closed again at the end of the war. The fourth thermic facility, located in Canaan, Connecticut, was placed under the jurisdiction of the United States Atomic Energy Commission. The Alabama Metallurgical Corporation introduced a new silicothermic facility at its Selma, Alabama plant in 1959. However, both the Canaan and Selma plants discontinued operation during the late 1960's. In 1970, large scale thermic reduction of magnesium was reintroduced into the United States with the selection of the Magnetherm process by Alcoa for the facility in Addy, Washington.

Other thermic facilities, such as the Pidgeon or silicothermic process, had survived the post-World War II era in other countries and continue to operate today. This is true of the Pidgeon, horizontal retort process as operated by Chromasco Limited of Canada. Other processes, which include the carbothermic process, were abandoned in 1945 and have not been revived.

The Pidgeon, Magnetherm, and carbothermic processes, as examples of existing thermic technologies, are to be described and discussed in the subsequent sections to establish the current level of development of thermic magnesium production technology. The proposed Avery process, Parlee-Anderson liquid metal solvent process, and other metallothermic processes are also presented to establish the future potential of thermic magnesium technology.

4.5.1 Metallothermic Processes

A. Pidgeon Process

One of the first commercial applications of the silicothermic reduction method was developed by L. M. Pidgeon in 1942 in Canada, where this process which bears his name remains in operation(35,36). Pilot-plant studies published by Pidgeon and Alexander illustrate the early development of the horizontal retort ferrosilicon process(37). The specific design of the Pidgeon ferrosilicon reduction plant is also well documented in the literature(38). The general materials flow diagram of the Pidgeon process is outlined in Figure 4.5.1.1.

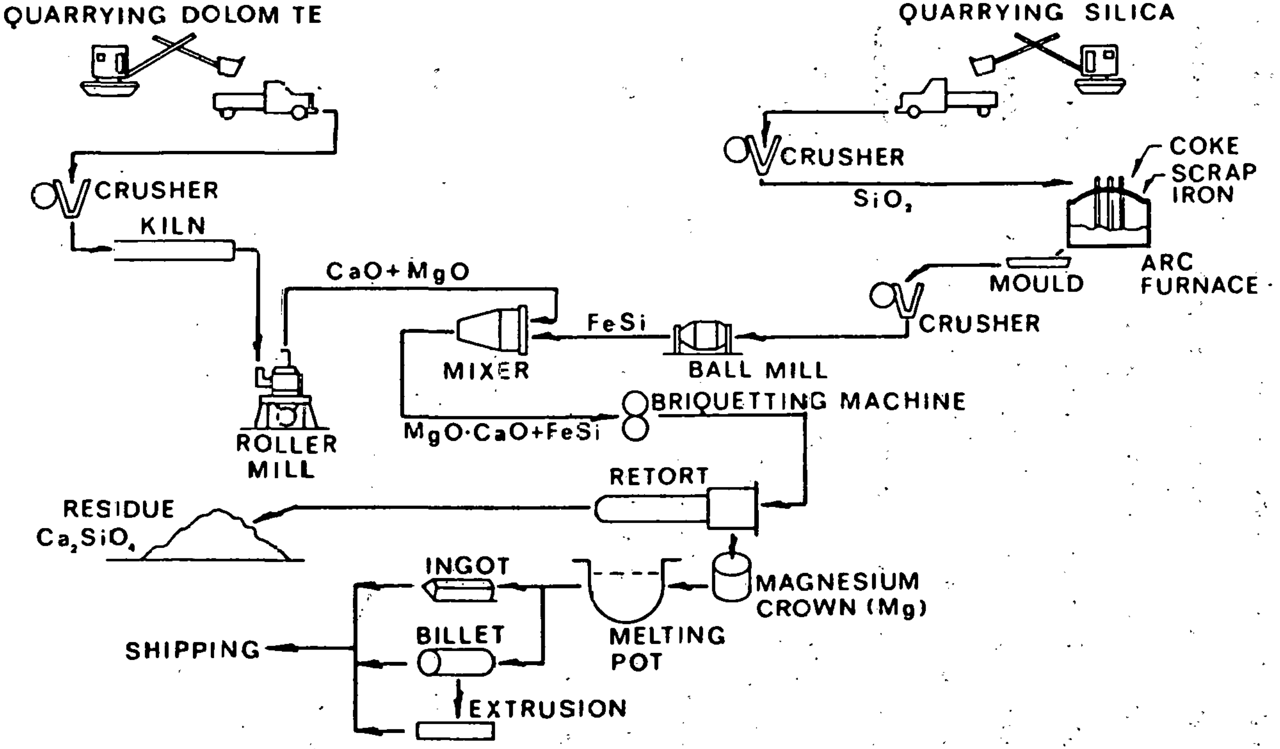

Figure 4.5.1.1: Material Flow in the Silicothermic Reduction (Pidgeon) Process.(7)

An excellent economic and technical evaluation of the silicothermic magnesium production process was completed by the United States Bureau of Mines in 1965(5). This report describes in detail the operations of the Defense Plant Corporation facilities which employed the silicothermic process during World War II and includes specific designs for a hypothetical plant complete with raw material, energy, and major equipment requirements.

The silicothermic process, as generally practiced, uses as its raw material high-quality (preferably 98 percent pure) dolomite. The dolomite is calcined in a rotary kiln to produce dolime. After being crushed, the dolime is mixed with 75-80 percent ferrosilicon in a ratio of about 5 to 1. This mixture is briquetted and charged in batches into tubular steel retorts which are externally heated to approximately 1200°C in furnaces using natural gas or electricity, Figure 4.5.1.2. Under a vacuum of 0.1 torr, the magnesium oxide is reduced and the magnesium content collected as crystalline crowns in the water-cooled head sections of the horizontal retort as also indicated in Figure 4.5.1.2. The reduction process has a cycle time of approximately 8 hours, after which the retort is cooled and the magnesium collected.

The excessive labor required to charge and discharge the retorts plus the low unit production capacity of the retorts seriously constrains productivity. This, combined with high maintenance costs for the retorts, results in very high production costs. For this reason, many of the Pidgeon magnesium facilities, including all of those in the United States, went out of production at the end of World War II. Those facilities which remain are able to compete by satisfying the demand for very high purity magnesium.

Careful consideration of the Pidgeon process, a fully developed technology, is important because it represents the foundation of subsequent metallothermic process developments. A clear understanding of the

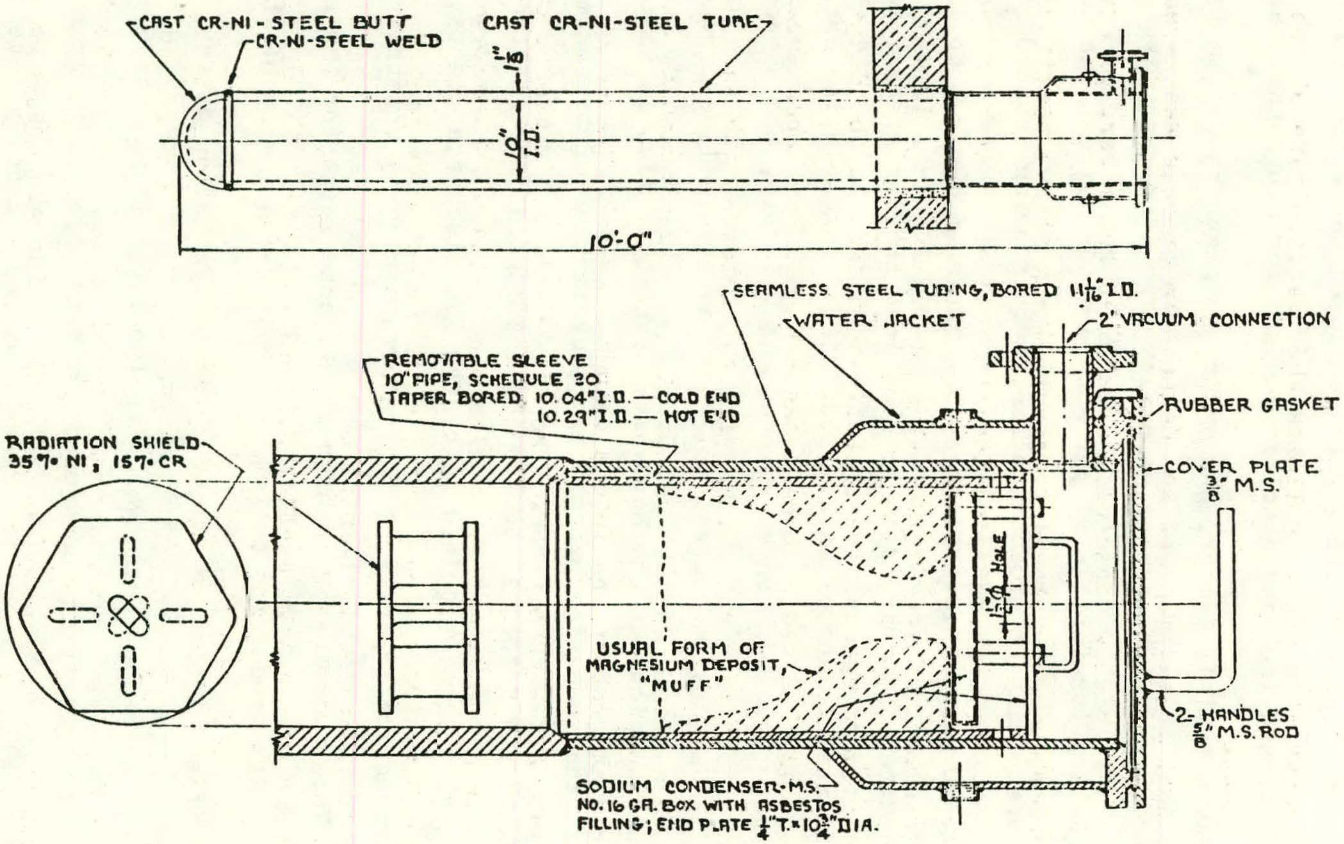

Figure 4.5.1.2: Silicothermic Furnace Retort.(38)

constraints of the Pidgeon process highlights the technical advances of its liquid phase counterpart, the Magnetherm process. For example, the Pidgeon process operates at a maximum temperature of only 1200°C because the metallic retorts are susceptible to slow collapse through creep while under vacuum. This temperature constraint severely limits the reaction rate of the Pidgeon silicothermic process.

The subsequent development of the Magnetherm process was based on technical innovations which successfully eliminated the retort materials of construction problem and heat transfer rate-limiting step. Specifically, the Magnetherm technology consists of a carbon lined furnace which operates at 1600°C and allows the silicothermic reaction to proceed in a liquid phase.

Significant improvements have recently been made in the Pidgeon process(7). Chromasco Limited of Canada has replaced the labor intensive manual operation of charging and discharging the retorts with an operator driven, mechanized device. The 300 pounds of spent briquettes in each retort are now swept from the retort and into a vacuum conveying transport duct with a positive pressure air stream probe. The 350 pounds of briquette charge is fed mechanically into the retort via a wire mesh telescoping conveyor mounted on a steel boom. This innovation significantly reduces the labor requirement, provides improved cleaning of the retort between cycles, and provides a uniform, level, high quality briquette charge with reduced fines which optimizes reaction efficiency.

Additional innovations designed to improve the operating efficiency of thermic magnesium reduction processes will be discussed after all of the individual processes have been considered. These innovations, some of which have not been previously considered, represent potential solutions to some of the operational constraints of current thermic processes.

B. Magnetherm Process

The Magnetherm process, which is also based on the thermal reduction of calcined dolomite with silicon, differs from the Pidgeon process in three fundamental regards(39,40):

a) The heat required to promote the reaction is produced within the furnace by direct electrical resistance heating of the slag versus the external heating of the Pidgeon retort.

b) The charge is molten.

c) The 7.5 tons/day production capacity of currently operating Magnetherm furnaces is greater than 4 times that of a typical Pidgeon furnace with 40 retorts.

A major obstacle to the initial development of the Magnetherm process was the 2130°C melting point of the dicalcium silicate slag resulting from the reaction of dolomite and silicon. This problem was eliminated with the addition of alumina or bauxite as a flux to the slag. The lime silicoaluminate slag which is formed has a reduced melting point of 1500°C. The overall reaction is as described in the following equation:

$$2(CaO\cdot MgO) + (xFe)Si + nAl_2O_3 \rightarrow 2CaO\cdot SiO_2,nAl_2O_3(\ell) + xFe(\ell) + 2Mg(g)$$

This low melting slag, containing unreacted ferrosilicon, created a materials of construction problem for the furnace lining since the use of alumina, silica, and lime would result in fluxing losses. The furnace lining currently used consists of tightly fitted carbon blocks.

The Magnetherm furnace is currently operated in a batch mode at about 1550°C and a pressure of roughly 35 mm Hg(8,9,41,42). A typical furnace has a capacity of 22,000 pounds of reactive materials containing 17 percent magnesium.

During the 20-hour operating cycle, ferrosilicon is fed continuously to the furnace from evacuated internal storage bins while dolime and alumina are fed at a rate of 20 batches per hour from similar bins above the furnace, Figure 4.5.1.3. After about 8 hours, or when the furnace is filled with slag, the electric power is reduced, the vacuum is broken, and the slag plus residual ferrosilicon are poured through a tap hole. This minor tapping operation is complete when the slag level in the furnace has been lowered to the upper level of the graphite electrode. The furnace is again evacuated, and a second loading cycle begins. At the end of this 9.5 hour cycle the furnace is again tapped to remove the slag. During this major tapping operation the condenser-crucible unit is also removed and replaced with a clean condenser and empty crucible. The total 20 hour cycle is repeated while the magnesium from the crucible is remelted, refined to remove calcium plus oxides, and cast as ingots. The complete flowsheet of the Magnetherm process is outlined in Figure 4.5.1.3.

Two by-products are produced by the magnethermic reduction process: lime silico-aluminate slag and low-grade (18-20% silicon) ferrosilicon alloy. The two by-products are separated in a ladle where 50 percent of the heavier ferrosilicon settles out of the slag at the bottom. The slag is poured off the top of the ladle and water cooled to produced a granular material. This granular slag has a minor market value as a binder in the cement industry. The low-grade ferrosilicon can be used in steelmaking or recycled to the ferrosilicon furnace.

The Magnetherm process, while offering significant advantages over the Pidgeon process, is also constrained by some of the same factors. For example, both are batch processes and are conducted under vacuum. The vacuum

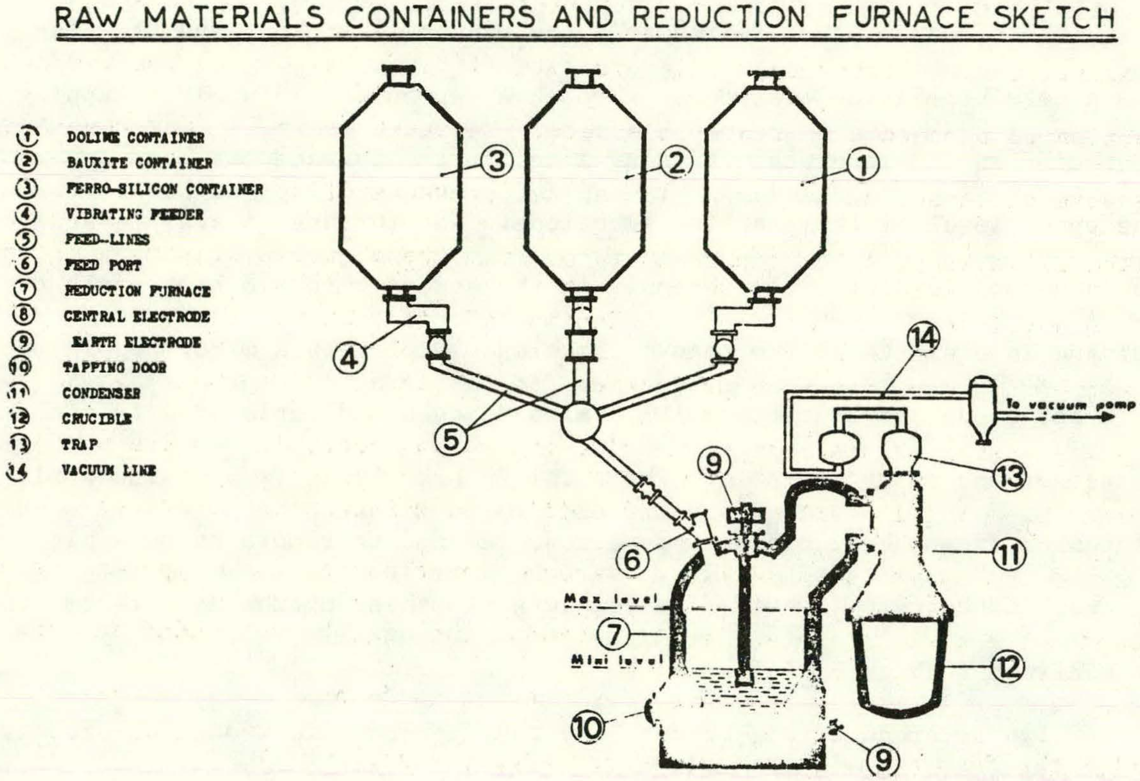

Figure 4.5.1.3: The Magnetherm Process: Raw Materials Containers and Reduction Furnace.(9)

system is that part of the condenser system which enhances the pressure differential driving force which is used to induce the magnesium vapor to leave the furnace and the critical reaction zone at the surface of the slag. The success of the distillation process depends upon maintaining the maximum differential between the magnesium vapor pressure above the reactants and the equilibrium vapor pressure. This pressure differential allows the reduction reaction to proceed at a reasonable rate; the reaction is blocked when this pressure differential is zero. The actual pressure differential is determined by the efficiency of the condenser into which the magnesium vapor enters via the vacuum line from the furnace. Because of air leaks in the vacuum system, oxygen enters the evacuated production and condenser units and reoxidizes the magnesium vapor. This magnesium oxide enters and contaminates the condenser, thereby reducing its efficiency and ability to maintain the critical magnesium vapor pressure differential. Vacuum operations of this type are usually closed batch systems. Specifically, production must be suspended and the vacuum broken to remove the slag, replace the condenser—crucible unit, and refill the feed material and reductant supply bins.

As in the Pidgeon process, it is the upper limit placed on the operating temperature which constrains the overall efficiency and productivity of the Magnetherm process. The maximum operating temperature constraint is partially determined by the onset of secondary carbothermic reactions within the furnace involving the graphite hearth and central electrode(40). Secondly, when ferrosilicon reductant is added to the surface of the slag, the reduction reaction proceeds rapidly. In the partial vacuum of the furnace the magnesium vapor boils off violently from the surface of the charge carrying slag particles with it. At 1550°C, the reaction settles down quickly as the silicon content of the reductant declines. This minimizes the slag particle carry-over into the condenser. Increasing the operating temperature while maintaining the low operating pressure would result in excessive slag carry-over and contamination of the condenser and magnesium metal. Furthermore, an operating temperature much in excess of 1550°C would reduce the viscosity of the slag and consequently, disrupt the existing convective flow pattern. The existing slag flow acts to transport heat away from the electrode and to the surface of the slag. The radial surface flow of the slag also extends the surface residence time of the denser molten ferrosilicon phase. This permits the ferrosilicon droplet to react more fully with the magnesium oxide component of the liquid slag before this droplet sinks deep into the slag where the head pressure of the slag will retard the evolution of magnesium vapor.

Conversion of the Magnetherm process from batch to continuous operation would eliminate the major factors constraining overall efficiency. This conversion should be the primary goal, whether or not the operating temperatures can be sufficiently increased, so as to eliminate the need for operation under vacuum. Conversion to continuous operation at a positive pressure would significantly reduce energy consumption and labor requirements, substantially increase the production capacity of the reduction unit, and reduce both capital and operating cost requirements.

Societe Francaise d'Electrometallurgie (SOFREM), the owner of the Magnetherm process, has made substantial technical improvements over the last 5 years(9). Furnace operations have been computerized and a pump-vacuum regulation system has been developed as part of a new, more productive, condensing unit. As a result, significant improvements have been made in the daily production rate, and raw material, energy, and labor requirements have been reduced. SOFREM is also working on the development of a suitable

3-phase power source which would supply approximately 10,000 KW of power(41). This development would represent a significant improvement in the production capacity of the standard reduction furnace.

A Japanese concern has also recently announced impressive results concerning efforts to expand the productivity of the Magnetherm process(43). It is reported that productivity 2 to 3 times that of the current Magnetherm furnace (7.5 ton/day) has already been obtained. It is also suggested that a vacuum electric reduction furnace with a capacity of 30 to 50 tons of magnesium per day will be in operation "before long".

While the developments discussed above significantly enhance the competitive position of the Magnetherm process, the batch operation constraint has not been removed. These developments are merely directed towards scale-up of the present process. The problem of operating under vacuum remains, including extensive down-time, and high labor and energy requirements. Some suggested potential improvements in thermic magnesium processes will be presented in a subsequent section following the discussion of all relevant processes.

C. Other Metallothermic Processes

Technically, the metallothermic process proposed by Julian Avery is a modified version of the SOFREM Magnetherm process(44). Avery proposes to operate the thermic reduction process at or approaching atmospheric pressure with the possible use of an inert carrier gas. If this could be accomplished, leakage of air and the attendant magnesium oxide formation and condenser fouling problems would be much reduced. This would reduce the frequency with which the condenser-crucible unit must currently be serviced. The overall effect would not only be a substantial increase in production due to increased metal recovery and operating time, but also a major decrease in labor requirements. Furthermore, the potential combination of increased recovery of magnesium as ingot due to the reduction in losses to magnesium oxide formation and the increase in productivity due to continuous operation would significantly reduce the energy requirement per unit of product.

The magnesium metal production rate of the metallothermic process is a function of the efficiency with which the magnesium vapor is transported from the furnace volume above the slag to the condenser. As one possibility, Avery has proposed that an inert gas sweep be used to carry the magnesium vapor from the furnace to the adjoining condenser. For reactions such as that of the Magnetherm process with a magnesium vapor pressure of 0.1 atmospheres, a massive flow of inert gas would be required (10 times that of the magnesium vapor). Techniques would need to be developed to recycle this gas, and to condense all the magnesium from it.

Avery also proposes to enhance the mass transfer mechanism between the furnace and condenser by increasing the partial pressure of the magnesium vapor to beyond 0.5 atmospheres. This can be accomplished by adjusting the combination of reductant, raw material, and slag composition without increasing the operating temperature above 1600°C. The recommended reducing agents are high silicon and aluminum-silicon alloys while the preferred feed materials include dolime combined with higher percentages of calcined magnesia. Slag compositions can then be altered so as to reduce the slag-metal ratio and thereby increase the production rate of a reactor of given size. While these improvements in the operation of the metallothermic furnace appear to be possible, they are yet to be demonstrated at the full commercial scale.

Conversion of the metallothermic reduction process to continuous operation may create operational difficulties for the currently used condenser system. Unless the oxide deposits which now contaminate the condenser can be eliminated, the condenser will continue to require periodic servicing. The presence of inert gas at atmospheric pressure could also present engineering and technical problems in a conventional condenser. Avery, recognizing these potential problems, has suggested that a splash condenser, such as that developed by New Jersey Zinc Company and illustrated in Figure 4.5.1.4 be considered(45).

The splash condenser would collect magnesium as a liquid, thereby facilitating its continuous or semi-continuous removal from the crucible. The only potential difficulty with the splash condenser is the efficient transport of the magnesium vapor from the furnace to the condenser. For example, while the proposed diffusion process is a viable transport mechanism, it does not take full advantage of the increased production capacity of the reduction unit. Avery has patented several magnesium condensers in this regard, one of which is illustrated in Figure 4.5.1.5(46).

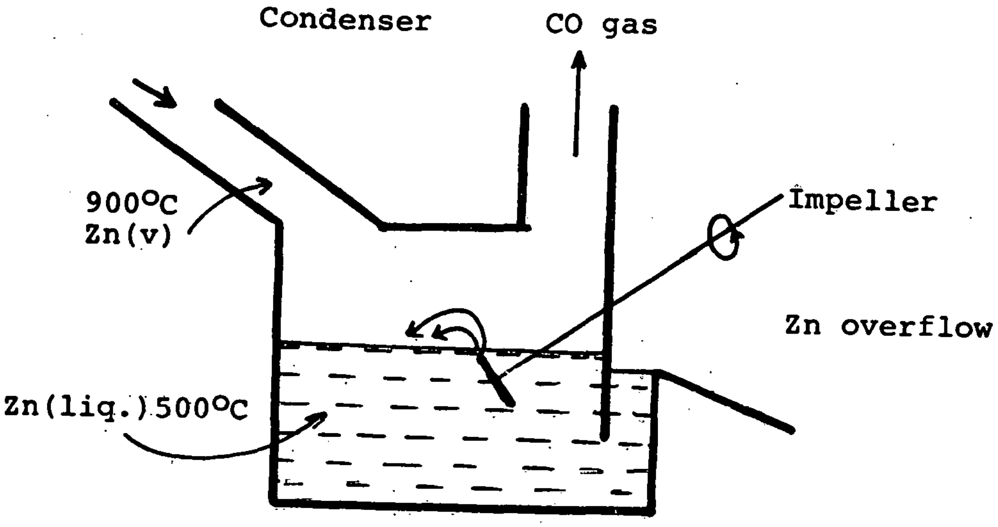

Figure 4.5.1.4: New Jersey Zinc Co. Splash Condenser.(27)

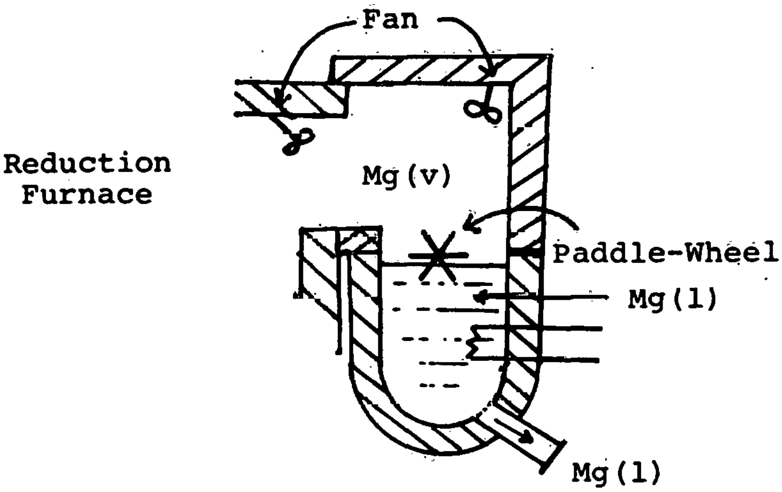

Figure 4.5.1.5: Avery's Paddle-Wheel Condenser.(46)

4.5.2 Carbothermic Processes

The carbothermic magnesium reduction process produces a gaseous oxide together with magnesium vapor by the following reaction:

$$MgO(s) + C(s) \rightleftarrows Mg(v) + CO(g)$$

The reaction is at equilibrium under standard conditions at approximately 1850°C. Unfortunately, at temperatures below 1850°C, the carbon monoxide, which is usually considered to be a reducing agent, acts as an oxidizing agent because of the high chemical activity of magnesium. It is this reoxidation of the magnesium vapor by carbon monoxide before the former can be condensed that poses a technical challenge.

The principal methods of preventing or inhibiting the reverse reaction are as follows:

1. The reaction products are shock-cooled through the critical temperature range, 1850° to 450°C.
2. The reactivity of the reaction products is reduced by dilution with an inert gas.
3. The magnesium vapor is separated from the carbon monoxide by absorbing it into another molten metal.

Shock-cooling with a gas coolant -- hydrogen, methane, or other hydrocarbon gases -- is actually a combination of methods 1 and 2. The condensate is a very finely divided dust consisting of metallic magnesium, magnesium oxide, carbon, and any other impurities found in the feed. Pure magnesium is distilled from this dust and subsequently cast as ingots. When molten metal absorption is used, the magnesium product is distilled from the absorbent metal which is then recycled.

Early attempts to reduce magnesium oxide carbothermically were unsuccessful because of the reverse reaction. The first successful method used to prevent the reverse reaction was shock-cooling with refrigerated hydrogen. Developed by F. J. Hansgrig in 1929, this process was used at plants in Austria, Korea, and Wales during World War II(47,48).

The Permanente plant, built in California during World War II with an annual capacity of 12,000 tons, was the most extensive development of the carbothermic process(49,50). This facility, based on the use of natural gas for shock-cooling condensation, was also the last application of the carbothermic process. The plant closed at the end of World War II.

An engineering and cost analysis of a hypothetical carbothermic plant based on the Permanente facility was completed by the U.S. Bureau of Mines in 1967(6). This report presents a detailed description of the unit operations of a hypothetical 24,000 ton per year facility, complete with flow diagrams and raw material, energy, and major equipment requirements.

In the carbothermic process, pellets of magnesium oxide and carbon react continuously in a closed, submerged-arc furnace operated at 1950° to 2050°C. The gaseous reaction products pass from the furnace through a port into a chilling cone where they are quenched to prevent the back reaction. Using bag filters, the solid product is recovered as a fine magnesium powder contaminated with carbon, magnesium oxide, and other charge impurities. After briquetting, the consolidated dust product is vacuum distilled to recover pure magnesium crystals which are melted and cast as ingots.

Quenching of the magnesium vapor has been accomplished on a commercial scale in the past with natural gas or hydrogen. The Bureau of Mines has also demonstrated the feasibility of using a molten metal, such as lead, as an effective quenching agent.(55)

Gas used in the quenching operation can be recycled to the quench after cooling and removal of the carbon monoxide produced with the magnesium. Such removal, accomplished by absorption or by bleed-off and replacement with fresh gas, is an expensive operation(51).

The carbothermic magnesium reduction process, an inherently efficient process as illustrated by Table 4.4.1, is critically constrained by the inefficiency of current condenser technology. Billiton Research B.V. of the Netherlands, and others have ongoing research and development programs, which report significant progress in this field. Potential innovations in magnesium vapor collection and process optimization from programs such as this could possibly result in the re-emergence of the carbothermic magnesium reduction process as an economically competitive technology. Recent advances are discussed in an earlier section dealing with current and ongoing research and development.

A. Parlee-Anderson Liquid Metal Solvent Process

The use of molten metal as a condensing medium for thermically produced magnesium vapor was first developed by J. D Hannawalt in 1943. In this process, the reduction products are cooled by direct contact with the molten metal - mercury, lead, or tin. The magnesium is recovered from the resulting solution by distillation to remove the more volatile metal.

Parlee and Anderson have recently evaluated the unique properties of liquid metal solvents and how these can be used advantageously in the development of novel ore reduction reactions(14,15). For a variety of reasons the liquid metal solvent reduction process may eliminate major disadvantages of the earlier carbothermic technology involving magnesium metal recovery.

The Parlee-Anderson process drives the oxidation reaction

$$MgO(s) + C(s) \rightleftarrows CO(g) + \underline{Mg}\ (\ell,\ \text{in solution})$$

to the right by lowering the activity of the magnesium. There is no tendency toward retro-reaction because the magnesium is retained in the liquid metal solvent while the carbon monoxide gas is removed.

Processes using this concept would involve two stages, a reaction stage and a separation stage. In the first stage, the magnesium oxide and carbon would react in an appropriate liquid metal solvent and carbon monoxide would be evolved. The product would be a molten magnesium alloy. This first stage is expected to have essentially the same type of thermal efficiency as a ferrosilicon electrothermic production process. The second stage would involve separation of the resulting alloy by distillation and collection of the magnesium product as a liquid. Not only would this make remelting unnecessary, but it would also have significant safety advantages. It is quite conceivable that the liquid magnesium from the condenser could be taken through a barometric leg for direct pigging.

Eckert and his colleagues at the University of Illinois have made extensive investigations of the thermodynamics of magnesium solvent metal systems and have developed both experimental and theoretical models(17-21). The reduction process in lead, tin, bismuth, antimony, and some solvent mixtures have been investigated. Preliminary designs for two magnesium plants using different solvent metals have been prepared(19). Schematic representations and rough cost estimates based on mid-1977 prices have been prepared based on laboratory scale equipment.

While the laboratory studies of the process have demonstrated its technical feasibility, quantitative statements which concern its economic feasibility are premature based on the current level of technical development. However, this innovative modification of the carbothermic magnesium reduction process warrants further study and development.

4.6 ASSESSMENT AND RECOMMENDATIONS

Introduced in 1961, the Magnetherm process represents the second generation of silicothermic technology and essentially supercedes the original Pidgeon process. While the Magnetherm process has continued its industrial development to date, as measured by its expansion of unit production capacity from 2.5 to 7.5 tons per day, it continues to operate subject to the following constraints:

1. a maximum operating temperature of approximately 1650°C;
2. a reduction furnace vacuum requirement of 25 mm Hg;
3. a 20 hour batch operating cycle;
4. a condenser technology which requires daily servicing with 20 percent downtime due to magnesium oxide fouling;
5. a lack of basic information concerning the actual rate determining mechanisms.

In the following sections, the constraints of current processes are assessed and recommendations for future work are made for existing and proposed technologies.

4.6.1 Operating Temperature Range

Because the partial pressure of magnesium vapor is low at current operating temperatures, a vacuum system is required to achieve adequate production rates with all existing metallothermic processes. If an operating temperature sufficient to generate magnesium vapor at a pressure exceeding one atmosphere could be attained, it is likely that there would be no need for the vacuum system. With such a substantial payoff it is very important that every effort be made to extend the operating temperature range.

However, increasing temperature is not an easy task. A solid slag layer must be maintained to protect the reaction crucible and this currently prohibits heating the slag much above 1650°C. Other slag compositions could be used. In any case, going to much higher temperatures would require major furnace redesign.

4.6.2 Reduction Kinetics

The basic thermal reduction unit developed and operated by SOFREM is depicted in Figure 4.5.1.3. Very little information is available in the open literature concerning the kinetics of this process other than the general design of the furnace, approximate operating temperature, composition of the slag and feed materials, and the batch cycle time. Figure 4.5.1.3 also illustrates the maximum and minimum permissible slag levels and indicates that the furnace hearth forms one of the electrodes while the other is fixed vertically from the furnace ceiling.

The original Magnetherm patent indicates that when fritted dolomite and ferrosilicon are introduced as particles (2 to 20 mm in size) into the slag, the reaction takes place in the liquid phase(52). If calcined dolime at ambient temperature is charged to the surface of the liquid slag at 1500°C, a violent liberation of gas results which carries slag particles into the condenser and contaminates the condenser and collected magnesium metal. Alternatively, if the calcined dolime is introduced hot at 800°C, all the feed materials can be added simultaneously to the slag at 1500°C. Current practice is that the raw materials be introduced in two stages: (1) the calcined dolime and alumina are dissolved in the slag, and (2) the ferrosilicon is then added to liberate the magnesium vapor. The addition of ferrosilicon must also be carefully controlled to avoid producing surges of magnesium vapor which can exceed condensing capacity and subsequently invade and plug the vacuum pipes.

It is reasonable to assume based on the instantaneous and violent evolution of magnesium from the surface of the slag that the reduction reaction goes quickly to completion within the first few inches of the slag surface. Magnesium vapor bubbles produced at greater slag depths either float to or are carried to the surface by natural convection or slag "roll-over"(8). Natural convection within the slag also supplies heat to the surface reaction zone from the hot zone associated with the submerged electrode.

High grade ferrosilicon reductant added to the surface of the melt forms an insoluble second liquid metal phase which sinks as globules through the less dense slag. As the ferrosilicon sinks it reacts to produce magnesium vapor and becomes an increasingly denser, lower-grade ferrosilicon globule as its silicon content decreases. A residual low-grade ferrosilicon alloy of roughly 20 percent silicon is produced and accumulates within the furnace. It is much denser than the molten slag and tends to settle at the bottom of the furnace.

Based on the above discussion, the optimum magnesium thermic reduction furnace design should minimize the concentration of residual reductant in the potentially most active reaction zone at the surface of the slag, utilize the hot zone as the primary reaction zone, and simultaneously minimize the amount of molten material which must be continuously heated. The latter goal can be accomplished by converting the present batch process to a continuous one. This would require the continuous removal of slag and collection of magnesium. Potential solutions to these present constraints will be considered in subsequent sections following the discussion of optimum furnace design.

4.6.3 Furnace Redesign

If it is assumed that the reduction process can be converted from batch to continuous operation, complete furnace redesign will be required to accommodate continuous slag removal and magnesium metal collection. Given these potential operating conditions, the possibility exists for creating a continuous flow-through reduction reaction zone. Specifically, the task would be to design a furnace with a reaction zone into which slag containing feed material and high grade reductant are top fed. Slag and residual reductant would exit from the bottom. In combination with an appropriate magnesium condenser, this would convert the current batch process to continuous operation with a commensurate increase in operating efficiency.

To supply sufficient heat to control the temperature of the molten slag and to drive the reaction to completion during the relatively short residence time of the reactants in the reaction zone will require substantial temperature gradients. The convection produced by these gradients, rather than being a detriment, may be exploited to enhance mass transport.

Recent developments in the computer modelling of electroslag refining and welding processes could be adapted and applied to this proposed flow-through reaction zone to quantitatively determine the temperature maps and stream-line patterns of the melt.(53,54) This information would greatly assist the design and optimization of the electrode arrangement and subsequent production efficiency.

In summary, then, to increase production a primary goal will be to achieve an operating temperature sufficient to produce magnesium vapor of greater than atmospheric pressure which would facilitate continuous operation.

4.6.4 Slag Removal

The current Magnetherm process requires that production be periodically interrupted and the operating vacuum be broken for slag removal. In practice, a solid plug is bored out (see Figure 4.5.13) and the excess slag drained into a settling pot. After the slag level in the furnace has returned to its lower level, the tap hole is plugged and the system evacuated. The slag removal operation, with simultaneous metal harvesting, results in a 2.5 hour shut-down period for each 20 hour operating cycle. The elimination of this periodic slag removal requirement would provide an immediate 12 to 15 percent direct increase in daily production rate before any of the subsequent improvements are considered. This improvement could permit continuous operation at optimum production efficiency with significant reductions in total labor requirements. Furthermore, if atmospheric or near-atmospheric pressure operation could be achieved, the slag could be removed, in principle, by a siphon arrangement, a bottom valve, or simply by tilting the reduction chamber to let the slag and heavy ferrosilicon residual reductant flow out periodically or continuously.

4.6.5 Continuous Magnesium Collection

The Magnetherm process currently uses a condenser/crucible unit for magnesium metal collection as illustrated in Figure 4.5.13. The condenser consists of a large diameter tube in which the magnesium vapor condenses as a liquid. The liquid magnesium runs down the walls of the condenser and collects in a steel crucible where it solidifies. At the end of the 20 hour production cycle the condenser/crucible unit is disconnnected from the furnace and is replaced by a clean condenser and empty crucible. The magnesium from the crucible is collected while the contaminated condenser is cleaned and serviced. Such a condenser/crucible arrangement and batch operation procedure must be replaced if continuous operation of the thermic magnesium reduction system is to be realized.

The condensation step in magnesium production is an important rate limiting factor and will become even more so as operating pressure is increased. Improved condensation technology is essential to improving the technology and economics of metallothermic reduction processes. Work is needed on improving conventional condensers and spray condensers such as those that have been proposed (Figure 4.5.14 and 4.5.15).

What is needed is a condenser that:

1. Collects the magnesium metal as a liquid and maintains a low equilibrium vapor pressure.
2. Has a large surface area to enhance condensation.
3. Is close to the source of magnesium vapor.
4. Does not experience a degradation of efficiency during the course of operating.

4.6.6 Critical Assessment of the Current State of the Art

Since World War II, commercial development of thermochemical processes for the reduction of magnesium has been restricted to metallothermic technology; the use of carbothermic technology ceased in 1945. Current metallothermic technology as represented by the Magnetherm process evolved from the original Pidgeon process. Both of these processes are dependent upon the same reductant and operate on a relatively small scale, producing a solid magnesium product at reduced pressure via a batch operation.

The principal factor constraining the operational efficiency of the current Magnetherm process is the vacuum requirement of the metal collection system. Specifically, the vacuum accentuates the leakage of air into the system. The oxygen and nitrogen in the air reacts with the cooling magnesium vapor to form magnesium oxide and nitride. This product consumes roughly a fifth of the magnesium produced and contaminates the condenser. The contamination of the condenser is so extensive as to require daily removal and servicing. This labor intensive operation further degrades the operational efficiency of the metallothermic process.

The vacuum requirement of the Magnetherm system also dictates that the process be operated in batch mode. The vacuum must be broken twice per production cycle to remove the slag. It is during the second process interuption that the condenser/crucible arrangement is also replaced and the reductant and feed material bins are refilled. These operations result in daily downtime in excess of 15 percent.

The elimination of the vacuum requirement would result in roughly a 25 percent increase in magnesium recovery with a corresponding increase in energy efficiency at no additional cost. Subsequent conversion to continuous operation would provide a 15 percent increase in production capacity with corresponding reductions in labor requirements. Such significant payoffs in terms of production improvements underscore the current inefficiencies of metallothermic magnesium technology.

Condenser efficiency also seriously constrains current operations. Reductant and feed material charging rates must be carefully monitored to avoid generating surges in the magnesium vapor production rate. These magnesium waves cannot be accommodated by the limited condensing capacity of current condensers and pass through to the vacuum pipes which subsequently become plugged, causing shut-down of the process.

The design of the reduction furnace is also inherently inefficient. Specifically, the heat source is at the bottom of the furnace while the principal reaction zone is at the surface of the slag. As the reduction process proceeds and the slag level rises within the furnace, these two critical zones become more and more separated. The process is thereby constrained by the convective flow of heat to the reaction zone.

Magnesium metallothermic process development also suffers from a lack of adequate thermodynamic and kinetic data. Improvements in the reduction reaction based on the selection of the optimum feed material, reductant, slag mix would amplify all other process improvements.

If the magnesium metallothermic process is to remain competitive, radical innovations will be required to improve the current technology. The primary goal of research in this area must be to eliminate the vacuum requirement of the system and to convert the process from batch to continuous operation.

4.6.7 Recommendations for Future Work

4.6.7.1 Reductants and Raw Materials

The choice of the reductant to be used in the thermochemical reduction of magnesium is a major factor in the determination of operating cost and energy efficiency. The specific combination of reductant and feed materials at a given operating temperature uniquely determines the composition and volume of the slag, the reaction rate, and the equilibrium vapor pressure of the magnesium produced. There currently exists a serious lack of available data concerning the kinetics and thermodynamics of thermochemical reduction of magnesium oxides with various reductants. The limited experimental data which do exist for various reductants usually disagree with calculated values by an unacceptable margin(5). The selection of optimum material-reductant-slag combinations and development of improved thermochemical technologies will clearly require the development of an adequate data base.

RECOMMENDATION A1: *Make the necessary thermodynamic and kinetic measurements of the pyrometallurgical reduction reactions for the various reductant-raw material combinations over the temperature range of interest, up to 2800°C, to provide a data base of reaction rates, magnesium equilibrium vapor pressures, and activity coefficients for all reductant, raw material, and slag combinations.*

RECOMMENDATION A2: *Determine and evaluate the kinetic relationship between operating temperature, reaction rate, and subsequent energy and operating efficiency for the various reductant-feed material combinations.*

Currently, ferrosilicon alloy is the preferred reductant for economic reasons. No other reductant is presently being used. However, thermodynamic data suggest that aluminum or aluminum alloys may be more efficient. The use of aluminum is currently constrained by price. Whether this situation will change is dependent upon the future development of new aluminum production systems -- such as a possible carbothermic process for aluminum silicon production -- or the technical feasibility of using low-grade aluminum alloys recovered from municipal refuse incineration plants.

RECOMMENDATION A3: *Investigate the availability and determine the purity of low-grade aluminum alloys available from municipal refuse incineration plants for use as an alternative metallothermic reductant.*

RECOMMENDATION A4: *Investigate the current level of development of carbothermic processes for aluminum-silicon production. Determine the feasibility of modifying this process to produce a lower grade, inexpensive aluminum-silicon alloy adequate for use in magnesium metallothermic processes.*

RECOMMENDATION A5: *Identify and evaluate the effects of the impurities found in aluminum-silicon and low-grade aluminum alloys on the production efficiency of the metallothermic reduction process. Ideally, the reaction slag would accommodate these impurities. If this is impractical, techniques for removing the specific undesirable impurities should be considered.*

Binary and ternary alloys such as aluminum-silicon and iron-silicon-manganese have been recommended as possible metallothermic reductants with the subsequent production of saleable by-product binary alloys beneath a silicate slag.

RECOMMENDATION A6: *Investigate the technical feasibility of co-production of magnesium and useful metallic master-alloys with metallothermic technology. Determine the economic impact of the alloy by-product, that is, its effect on operating and capital cost, and overall energy efficiency.*

4.6.7.2 Metallothermic Process Development

The production rate and efficiency of current metallothermic magnesium technologies is constrained by the vacuum requirements and inadequacies of condenser technology. The current magnesium vapor collection mechanism is based on the driving force of the magnesium vapor pressure differential between the furnace reaction zone and condenser surface. The entire furnace/condenser system is evacuated to facilitate this mass transport mechanism. The reduced pressure atmosphere in the condenser also significantly increases the condensation rate. Unfortunately, the reduced pressure also enhances the leakage of air into the system making possible the reverse reaction of the magnesium with oxygen. Magnesium metal losses result and the oxide formed coats the condenser and reduces its thermal efficiency. Furthermore, even with the partial vacuum, the current condenser is of only marginal efficiency unable to handle momentary surges in the magnesium vapor production rate.

Maintenance of the vacuum requires that the entire system be closed and therefore must be operated in batch mode. If the system could be operated at atmospheric pressure, metallothermic technology could be converted to continuous operation. Continuous process operation would require continuous magnesium metal collection and removal.

RECOMMENDATION B1: *Support the development of innovative efficient condenser concepts designed to operate at pressures approaching or exceeding one atmosphere. Possibilities include the use of inert carrier gas systems and liquid metal splash condensers.*

Conversion of the metallothermic system to continuous operation would also require the development of a continuous slag removal mechanism.

RECOMMENDATION B2: *Investigate the potential for modifying current furnace design to accommodate continuous slag removal using a barometric leg, gas-lift pump/siphon arrangement, or various other continuous or semi-continuous slag removal techniques.*

Assuming that continuous magnesium metal collection and slag removal can be achieved, the design concept of a continuous flow-through reduction unit becomes an important possibility. The reduction crucible would be redesigned to accommodate the selected reductant, feed material, slag composition, operating temperature, and potential innovations in slag removal and metal collection. A comprehensive study of the thermal and fluid dynamic characteristics of the molten slag would be required to optimize the design of the reduction unit and electrode arrangement.

RECOMMENDATION B3: *Develop mathematical and experimental models to establish the fluid flow, vapor transport and heat transfer characteristics of the basic metallothermic system.*

RECOMMENDATION B4: *Assess various continuous reactor designs based on the mathetmatical models of fluid flow and heat transfer phenomena. Construct laboratory scale experimental furnaces to verify the mathematical models.*

The scale-up of laboratory facilities to pilot plant or full commercial size is always a critical design problem. Therefore, it is important that the mathematical models for laboratory and intermediate size facilities accurately reflect the scaling characteristics of the process.

RECOMMENDATION B5: *Analyze the operating characteristics of laboratory and intermediate experimental metallothermic facilities to establish the sealing conditions and modify the mathematical models accordingly.*

4.6.7.3 Carbothermic Process Development

While the carbothermic magnesium production process has not been practiced since 1945, it is potentially the most energy efficient by far of all the processes considered here (see Table 4.4.1). Unfortunately, the reverse reaction of the co-products, magnesium vapor and carbon monoxide gas, severely constrains the production efficiency of this process. Recent efforts have centered on solving this metal collection problem.

One approach to minimizing the reverse reaction during condensation has been to reduce to a minimum the temperature at which the reduction reaction is conducted. A recent U.S. Patent suggests that the carbothermic process can be operated at as low as 1000°C in the presence of metallic catalysts(22). Under these conditions the reverse reaction of magnesium vapor and carbon monoxide to form magnesium oxide, which occurs between 1850°C and 450°C during the quenching stage of the standard carbothermic process, is minimized. A magnesium product of 95 percent purity has been reported with this process.

An alternative approach to collection of the carbothermic vapor product is rapid rate separation and cooling of the magnesium vapor and carbon monoxide gas coproducts. An innovative technique for accomplishing this separation and condensation has been suggested(24). This novel approach is based on the concept of gas phase separation during expansion through a divergent nozzle under conditions of underexpansion. The gases are both separated and rapidly cooled as they diverge from the nozzle exit at supersonic velocities. The collected magnesium product is reported to be of very high purity.

RECOMMENDATION C1: *Develop mathematical and experimental models to characterize the thermochemistry, vapor transport, and heat transfer phenomena of the basic carbothermic process.*

RECOMMENDATION C2: *Initiate a program to evaluate alternative innovative techniques designed to overcome limitations of the current carbothermic process, for example, with respect to magnesium vapor condensation and collection.*

The innovative carbothermic process developed by Parlee and Anderson avoids the characteristic reverse reaction by never allowing the magnesium product and carbon monoxide to come into contact(14-16). Specifically, the carbon monoxide gas rises from the charge while the magnesium product is removed in a molten metal solvent below the charge.

RECOMMENDATION C3: *Explore the further development of the liquid metal solvent process for the production of magnesium beyond the laboratory scale. The critical factors concerning solvent flow through the reactor, solvent recovery, and overall energy efficiency and cost effectiveness must be further studied and evaluated.*

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5. THE ECONOMICS OF EXPANDED MAGNESIUM PRODUCTION AND UTILIZATION

5.1 INTRODUCTION: MAGNESIUM IN PERSPECTIVE

The primary motivation for expanded use of magnesium is energy conservation in the transportation sector, where fuel economy is directly related to weight reduction. Magnesium, with a density two-thirds that of aluminum and roughly one-fifth that of ferrous materials, is the lightest commercially available material. It is this low density which renders magnesium particularly attractive for use in transportation applications where weight reduction can result in significant energy savings over the lifetime of the vehicle.

Magnesium could serve as a substitute for a wide range of materials, but its most attractive applications are as a substitute for many of the current automotive uses of die cast aluminum and for those components where light weight materials could be used to replace ferrous alloys. Table 5.1.1 summarizes the broad range of alternate automotive materials potentially available and the major weight reductions that could be achieved through the use of each. While some gains are available from dent resistant and high-strength, low-alloy steels, more significant gains in weight reduction in the 40 percent or more range are available from ultra high-strength steel, wrought and cast aluminum, plastics (reinforced or otherwise), and possibly superplastic zinc. The premier alternative automotive material with respect to weight reduction potential is magnesium. In die cast applications, magnesium competes primarily with aluminum, and to a certain extent with plastics. Magnesium and HSLA steels do not compete directly.

Table 5.1.1

Candidate Alternative Automotive Materials

	Percent Direct Weight Reduction Potential
Wrought Material	
Low Carbon Steel (LCS)	--
Dent Resistant Steels	10 to 20
High Strength/Low Alloy Steel	15 to 30
Ultra-High Strength Steel	40 to 50
Aluminum (Al)	50 to 60
Metal Castings	
Grey Iron	--
Al Die Casting	50 to 60
Al Permanent Mold Castings	50 to 60
Zinc Die Casting	10 to 40
Magnesium Die Casting	75
Plastics (Relative to LCS)	
Unidirectional Fiberglass Reinforced Polyester or Epoxy Resin	50
Sheet Molding Compound Random Fiberglass-Reinforced-Polyester Resin	35 to 50
Unidirectional Graphite Fiber Reinforced Epoxy Resin (Hybrid Reinforcement with Fiberglass, Where Possible)	60 to 70
Continuous Fiberglass Reinforced Nylon "STX" Hot Stampable Sheet	35

Adapted from: Proceedings of Conference on Basic Research Direction for Advanced Automotive Technology, U.S. Department of Transportation, Boston, April, 1979.

According to Table 5.1.1, the following weight reductions could be achieved by replacing 100 pounds of the current ferrous automotive material with the necessary amount of each material listed:

Material	Direct Weight Reduction (lbs)
HSLA steel	15 - 30
Aluminum	50 - 60
Graphite fiber reinforced composites	60 - 70
Magnesium	75

The critical question is whether the substitution of aluminum, magnesium, and plastics/composites will result in life cycle energy savings even though each of these materials requires much more energy to produce than does, for example, cast iron. The answer is a resounding "yes" as illustrated in Table 5.1.2 where the net life cycle energy credit available from substitution of light weight materials for cast iron has been calculated.

The net energy savings calculation, which is also given in gallons of gasoline saved per pound of each material used over the 100,000 mile life of the vehicle, includes an additional 50 percent indirect weight reduction available from vehicle redesign which takes full advantage of the direct weight reduction. The "bottom line" is that energy savings from increased gas mileage far outweigh the increased energy cost of producing the primary material. For example, the substitution of only 2 pounds of magnesium for ferrous components in an automobile saves nearly 1 gallon of gasoline per annum.

Table 5.1.2

Total Life Cycle Energy Savings Obtained by Substitution of Light Weight Materials for Cast Iron

Category	Aluminum	Magnesium	Plastics	Grey Iron
Energy to produce primary material[*] (BTU/lb)	110,290	144,400	45,000	8,100
Energy to recycle (BTU/lb)	2,776	2,865	-	2,982
(%) of recycled material	65	0	0	85
Total energy for production of material (BTU/lb)	40,400	144,400	45,000	3,750
Energy to produce castings, moldings, etc. (BTU/lb)	8,500	9,000	5,900	8,100
Total energy requirements (BTU/lb)	48,900	153,400	50,900	11,850
Net life cycle energy savings[+] (BTU/lb)	345,000	529,000	343,000	-
Equivalent gasoline savings (gal)	2.8	4.2	2.7	-

[+] Energy saving results from increased gas mileage attributable to light weight materials substitution for cast iron. This calculation assumes that 1 lb. of aluminum, plastics, and magnesium saves 2.25, 2.25, and 3.9 net lbs., respectively, when substituted for cast iron. This assumption is based on reported applications(1,2). The relationship between fuel economy and car inertia weight in 1979 specifies that a one pound reduction in weight conserves 1.4×10^{-5} gallons of gasoline per mile traveled. (One gallon of gasoline has a heat content of 125,000 Btu.)

[*] To avoid any possible confusion, all energy is given in kWh-thermal.

Note: Total weight savings attributable to light weight substitution consists of both direct and indirect weight reductions. "Indirect" weight reductions are those which may be retrieved through the interactive effects on the total vehicle design (e.g., reduced overall structural requirements). If only direct weight reductions are considered (e.g., as in Table 5.1.), weight reductions would be about 67 percent those considered herein.

If only 50 pounds of magnesium were to be used in a fleet of 10 million passenger cars, the net energy savings over the service lifetime of this fleet would exceed 2.1 billion gallons of gasoline. This is the net amount of energy saved after the total energy to produce the magnesium component has been accounted for.

The major issue concerning the future use of magnesium is economic viability. Magnesium is clearly the most energy efficient automotive material available and European automakers have more than adequately demonstrated its technical feasibility with more than 45 years of continuous use. It is the issue of price and availability which is currently, and has essentially always been, the limiting factor to expanded use of magnesium in automotive applications.

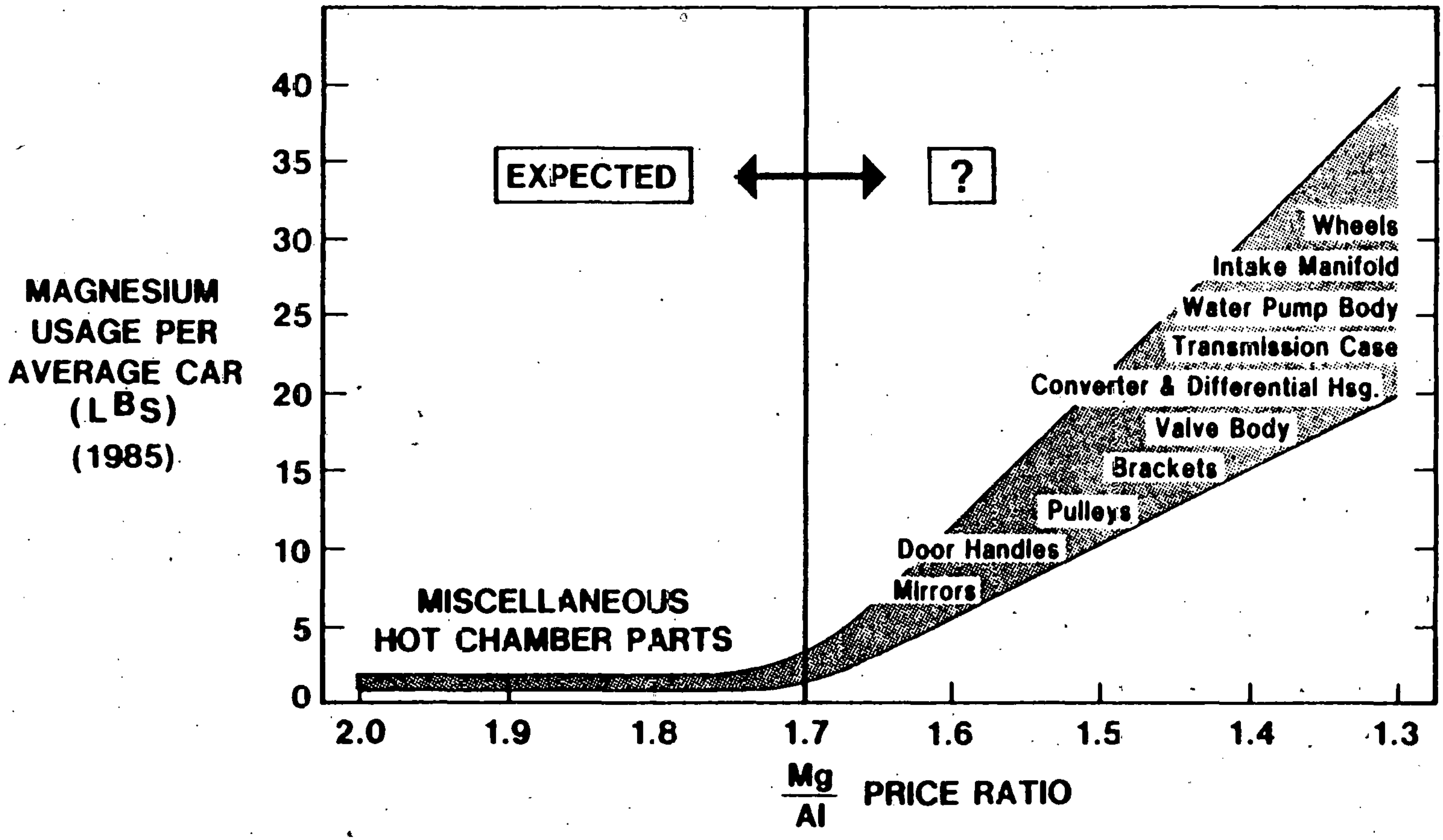
5.2 PAST AND PRESENT TRENDS IN THE PRICE OF MAGNESIUM

Magnesium is most competitive in automotive applications as a casting. In this market it competes primarily with die cast aluminum as a substitute for heavier ferrous auto components. Consequently, the demand for magnesium in automotive applications is determined in the first order by its price relative to aluminum.

The potential use of magnesium as a function of the price of aluminum has been quantified by the automotive industry. This relationship, as illustrated in Figure 5.2.1, was presented by Ford in 1977 as representing the possible levels of magnesium usage per car by 1985 as a function of the magnesium to aluminum price ratio(3). Since 1977, magnesium has become more attractive to automakers because of the U.S. Corporate Average Fuel

Figure 5.2.1:

POSSIBLE MAGNESIUM USAGE BY 1985 AS A FUNCTION OF Mg:Al PRICE RATIO



Source: M. Holland, Ford Motor Company(2).

Economy (CAFE) requirements, added consumer pressure for improved mileage, and its declining price ratio with respect to aluminum. This positive pressure would tend to cause the right half of the curve in Figure 5.2.1 to move upward. However, the average size and weight of the U.S. automobile is declining significantly thus requiring less light weight material per vehicle to meet mileage requirements. These two factors essentially offset each other which leaves Figure 5.2.1 unchanged and representative of the current automotive market potential for magnesium, assuming an appropriate 3 to 5 year testing, retooling, scale-up lag period.

Recent trends in the price of magnesium and aluminum are illustrated in Figure 5.2.2. For nearly two decades the price of aluminum remained fairly stable as this industry pursued market penetration and sales growth versus profit maximization. Even during the early 1970's, under President Nixon's mandatory wage and price guidelines, the U.S. list price of aluminum declined. It was not until 1973 and the Arab oil embargo, which coincided with the removal of the wage and price guidelines, that the price of aluminum began to rise. The aluminum industry reversed its pricing policy in favor of profit maximization late in 1977. However, by 1978 the U.S. aluminum industry found its list price tied to and constrained by President Carter's voluntary wage and price guidelines. Consequently, a two tiered world pricing system developed in aluminum as illustrated in Figure 5.2.2. The disparity between the London Metals Exchange and U.S. list price peaked earlier this year and has since reversed itself due to the current worldwide economic downturn.

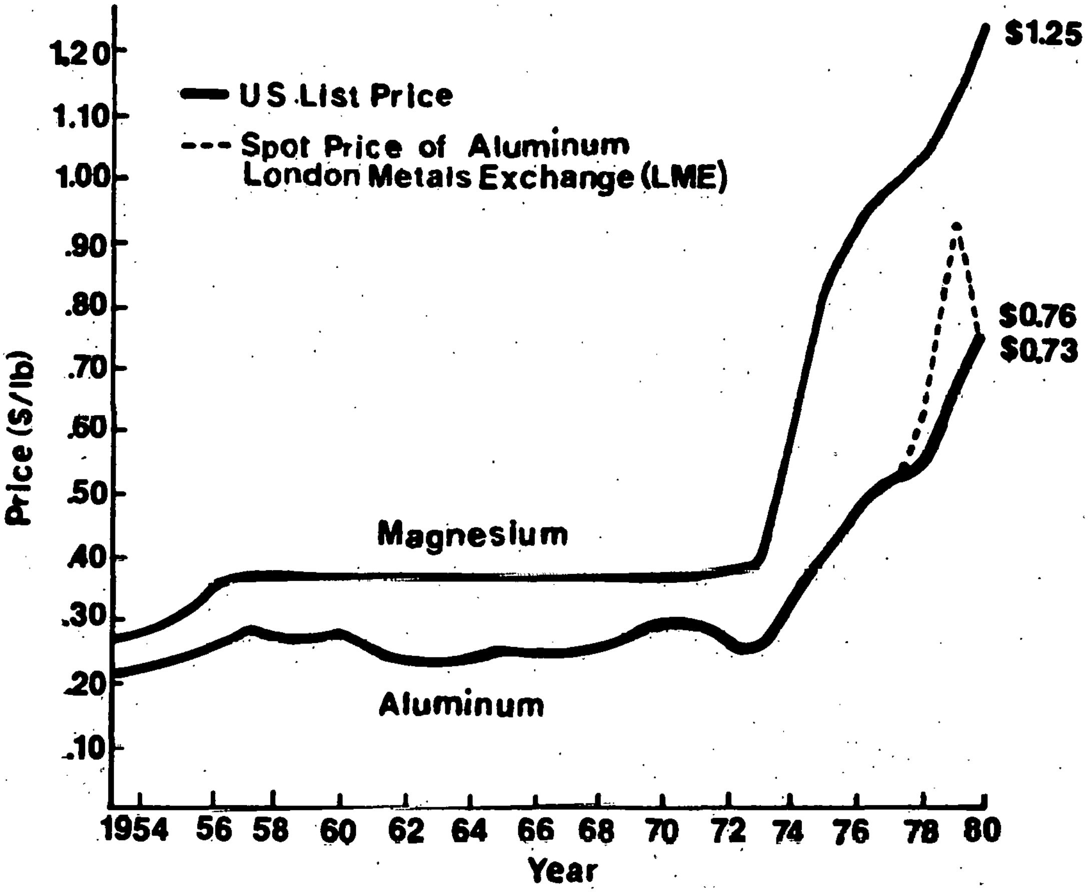


Figure 5.2.2: Price of Magnesium and Aluminum.

The list price of magnesium began to rise in 1970 after having remained constant throughout the 1960's. However, price increases were constrained by mandatory wage and price guidelines during the early 1970's. In 1973, when the wage and price guidelines were removed and the Arab oil embargo got underway, the price of magnesium rose sharply.

It has been suggested that the rapid rise in the price of magnesium between 1973 and 1975 was due to two distinct factors. The first was the obvious increase in the price of energy which began in 1973. The second factor was the change which occurred in the pricing policy of the magnesium industry which was due to the impending change in the nature of the industry itself. Specifically, in 1970, magnesium production capacity in the United States was expected to rapidly expand by 100 to 200 percent with the entry of several new large-scale producers. This event was expected to convert the U.S. magnesium industry from a single source condition which existed in 1969 to an oligopolistic or even fully competitive condition. In this situation, where large-scale multiple entry into a sole supplier industry is imminent, the optimum economic strategy of the existing firm or firms is to initiate a short-term profit maximizing policy. Such a shift in pricing policy would cause the price elasticities of demand for the product to rise to a level of -1.0 or greater. An econometric analysis of the magnesium market identified just such a shift in the price elasticities of demand for magnesium between the early and mid 1970's(4). Price elasticities of demand which were consistently less than -1.0 during the early 1970's were found to be consistently greater than -1.0 in 1976 thereby identifying a specific shift in pricing policy by the magnesium industry during this period.

By 1977, the price of magnesium had more than doubled and was reported to be at the reinvestment level. The price of magnesium has since risen moderately under the current voluntary wage and price guidelines.

The subsequent magnesium to aluminum price ratio is presented in Figure 5.2.3. During the 15 years following World War II, the price ratio never exceeded 1.3 to 1.0. Historically, its value has been consistently less than 1.6, a value which was first surpassed in 1974. Currently, the U.S. list price ratio of magnesium to aluminum has settled to a level of 1.64 after having peaked at more than 2 to 1 in 1976. At its current price relative to aluminum, magnesium is only marginally competitive with aluminum in automotive applications.

5.3 THE CURRENT TOTAL DEMAND FUNCTION FOR MAGNESIUM

Automotive applications, as illustrated in Figure 5.2.1, represent a tremendous market growth potential for magnesium if it can be made available at a price competitive with aluminum and other light weight materials. The critical question that remains is how the automotive market for magnesium will develop.

Figure 5.3.1 was first prepared in 1977 to assist in establishing the demand curve for magnesium(1). The total demand function for magnesium contains both an inelastic and elastic component. The inelastic portion of the demand curve represents the current non structural and special structural uses of magnesium. This includes alloying, chemical, metallurgical, and aerospace applications. The elastic portion of the demand curve represents the potential automotive demand for magnesium and is generated from the data available in Figure 5.2.1 based on a $0.48 per pound list price for aluminum

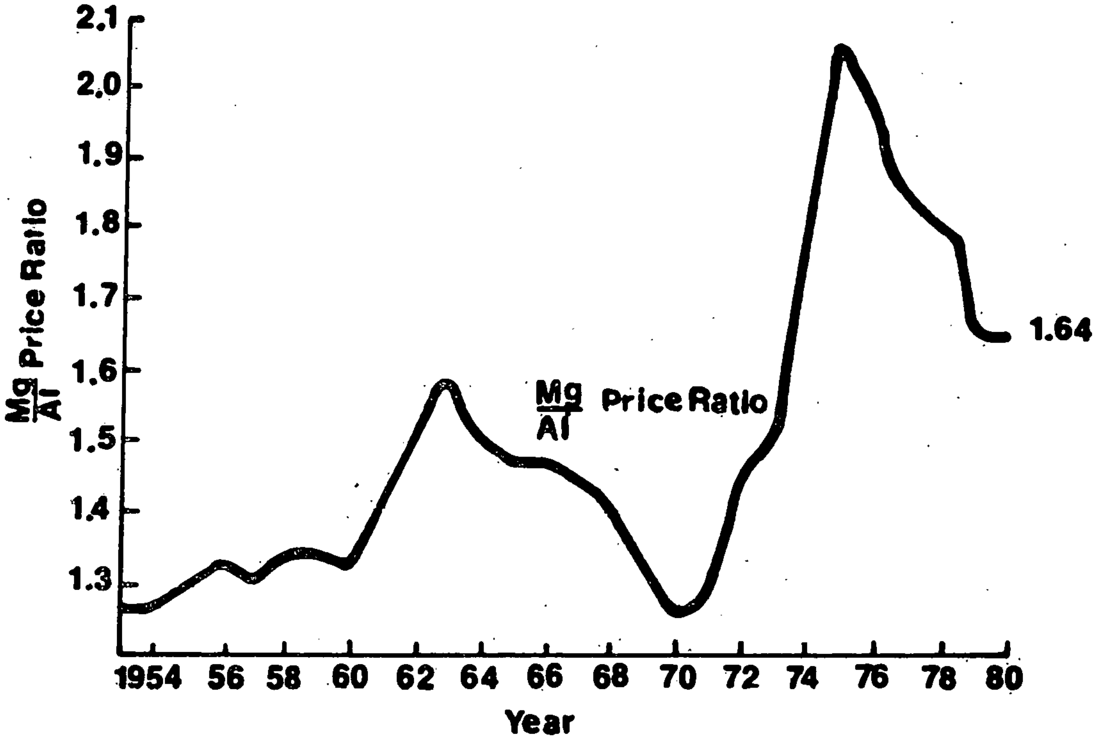


Figure 5.2.3: Magnesium to Aluminum Price Ratio (U.S. List Price).

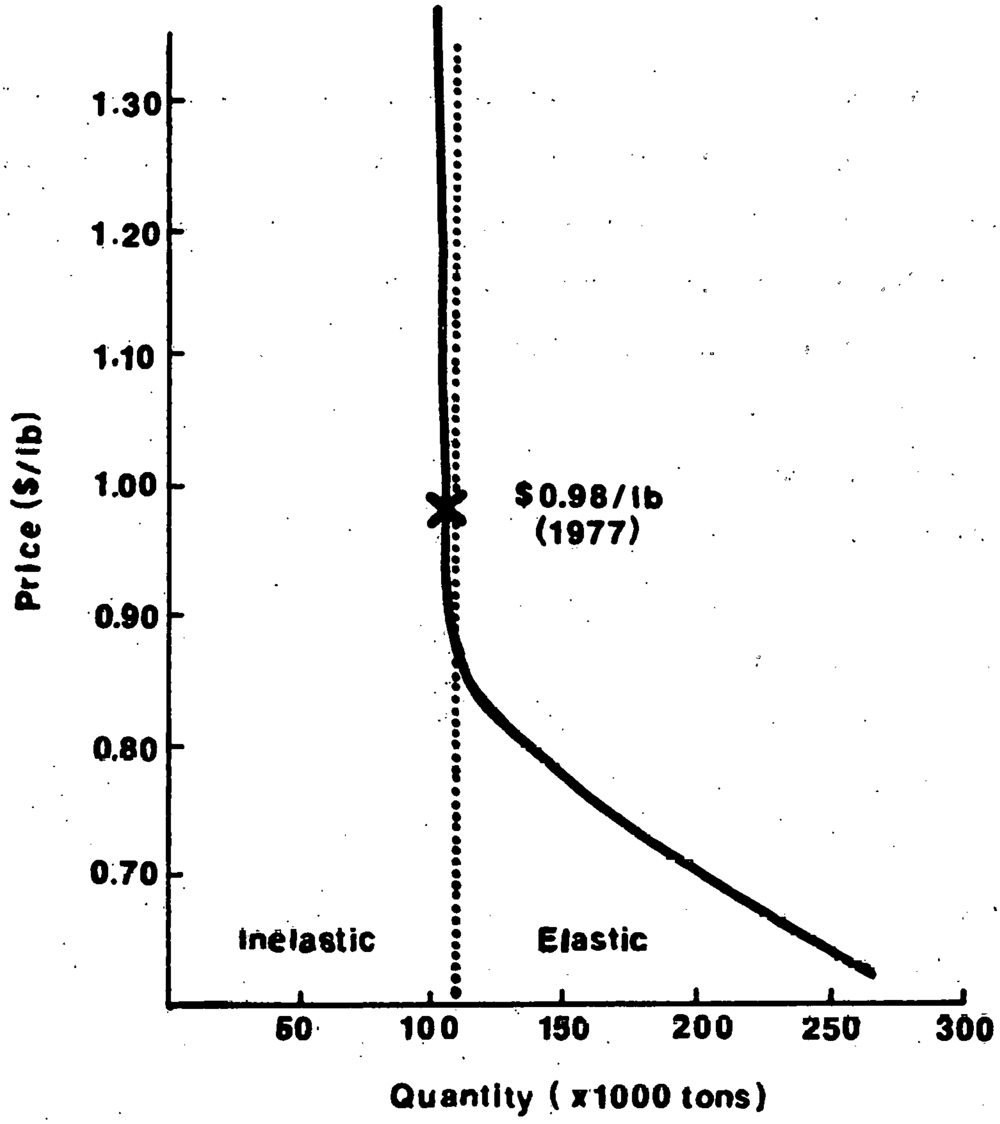


Figure 5.3.1: Total Magnesium Demand Function.

which prevailed in 1977. At that time the price of magnesium was $0.98 per pound which suggests that magnesium was priced out of the elastic automotive market.

If Figure 5.2.1 is representative of current automotive demand for magnesium, as suggested earlier, the elastic portion of the demand curve presented in Figure 5.3.1 can be revised to reflect the 1980 level of automotive demand using the current $0.76 per pound list price of aluminum. The result is presented in Figure 5.3.2. The inelastic portion of the demand curve is assumed to have remained essentially unchanged since 1977 which is substantiated by recent consumption patterns and trends. The elastic automotive portion of the demand curve has shifted upward to the level where magnesium, and especially die cast components, is now price competitive with aluminum at a price of $1.25 per pound.

While the literature has recorded numerous reports of the impending magnesium penetration of the automotive market over the last several decades, the data in Figure 5.3.2 suggests that the economic or price constraint has finally been satisfied for at least a small portion of the automotive market. The future growth of the automotive market for magnesium will be determined, as in the past, by the relative price of magnesium and aluminum. If the price ratio of magnesium to aluminum continues to decline, which would cause the elastic portion of the demand function to continue to rise, a U.S. automotive market for magnesium larger than current total U.S. consumption could be created.

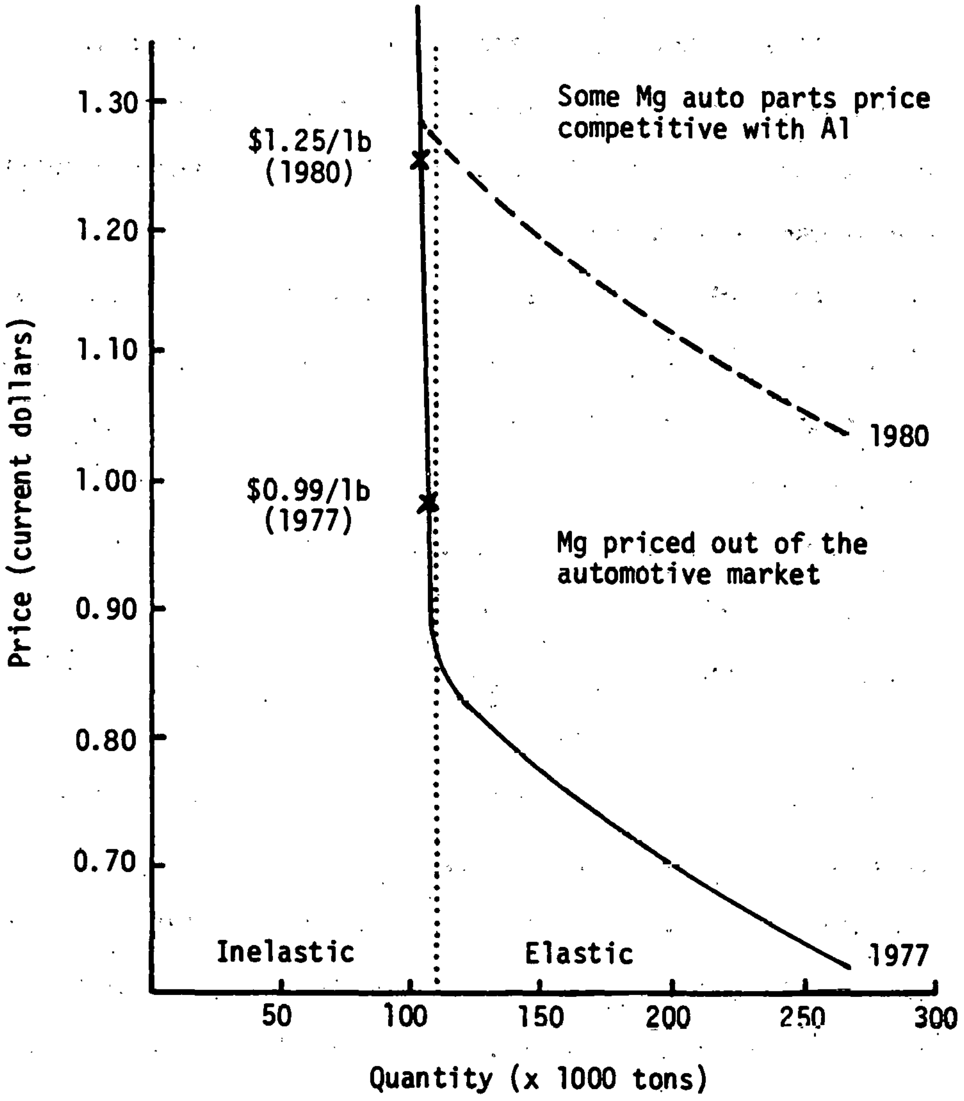


Figure 5.3.2: Total Magnesium Demand Function.

5.3.1 Constraints on the Magnesium to Aluminum Price Ratio

Figure 5.3.2 suggests that a 10 percent reduction in the price of magnesium relative to aluminum would create a U.S. automotive market for magnesium of roughly 75,000 tons per annum. Consequently, the critical question is whether there is room for such a reduction in the current 1.64 to 1.0 price ratio of magnesium to aluminum.

As recently as 1970 the price ratio of magnesium to aluminum was as low as 1.25, Figure 5.2.3. Its climb to more than 2 to 1 by 1975 cannot be fully justified in terms of technical factors alone due to the similarities of the technology employed for electrolytic production of magnesium and aluminum. A National Materials Advisory Board reached the same conclusion in 1975, when it reported that based on technology then available the cost of magnesium ingot should be no more than 25 to 40 percent higher than the cost of aluminum ingot(5).

As discussed earlier, a portion of the increase in the price of magnesium between 1973 and 1975 can be attributed to a shift in the pricing policy of the magnesium industry. This change in pricing policy has been calculated to have contributed between $0.13 and $0.30 per pound to the price of magnesium(4). This increase in the price of magnesium represents the difference between the historical trend in the price of magnesium relative to aluminum and the peak which occur in this ratio in 1975.

Since the mid 1970's, the price ratio of magnesium to aluminum has settled to its current level of 1.64 to 1.0. A 10 percent further reduction in the price of magnesium would reduce the current price ratio to 1.48. At this level the price ratio would be in basic agreement with its long term historical trend as recommended by the National Materials Advisory Board and as suggested by Figure 5.2.3.

The magnesium to aluminum price ratio appears to have established a new minimum value of roughly 1.65. The ratio was established early in 1980 and has been maintained through the last two major price increases in both magnesium and aluminum. The reason for this behavior is clearly illustrated in Figure 5.3.2. Any further decline in the price ratio of magnesium to aluminum would create a substantial automotive market for magnesium. However, the magnesium industry is currently operating at roughly 95 percent of capacity and, therefore, simply does not currently have the production capacity available to supply an expanded automotive market for magnesium. Consequently, magnesium is priced at the supply/demand equilibrium which leaves the automotive market marginally accessible to magnesium.

Under these conditions, the long term magnesium to aluminum price ratio can be expected to decline slowly as production capacity is expanded to meet the automotive demand for magnesium. However, there is little incentive for current magnesium producers to attempt to penetrate the automotive market due to the inelastic nature of the current non-automotive market for magnesium, Figure 5.3.2. Specifically, in the current inelastic market, the magnesium producers are relatively immune to price fluctuations. For example, the price of magnesium sold as an alloying agent is relatively insensitive to the price fluctuations of the alloy itself since it, magnesium, represents only a small fraction of the total cost of the alloy. If magnesium were to penetrate the automotive market, it would necessarily have to compete on a price basis with the other light weight materials in this extremely competitive market. The inelastic market for magnesium would become subject to these price fluctuations since it and the elastic automotive market cannot be effectively separated.

5.4 AN ECONOMIC ASSESSMENT OF MAGNESIUM PRODUCTION TECHNOLOGY

Magnesium penetration of the automotive market is expected to be a slow evolutionary process given the current industrial and economic structure of the U.S. and world magnesium industry. However, this need not be the case. The use of magnesium by the automotive industry would expand rapidly if magnesium were made available at a more attractive price, specifically, a price of less than 1.6 times the price of aluminum (Figures 5.2.1 and 5.3.2). Since the current magnesium industry is reluctant to price magnesium below a price ratio of 1.65 with aluminum, rapid penetration of the automotive market is unlikely to occur.

It appears that the necessary requirement for rapid penetration of the automotive market is entry into magnesium production by a new firm or firms with the specific strategy of pricing magnesium to compete with aluminum. This entry into magnesium production must also be of a sufficient scale to attract the automotive customer. If a part or parts are to be designated in magnesium, the automaker must be assured that sufficient material is available from multiple sources to accommodate the conversion to magnesium throughout the fleet consisting of millions of vehicles. It is the magnitude of this automotive market and the tremendous market growth potential that it potentially represents for magnesium which provides the motivation for large-scale entry.

The corporate decision to enter into magnesium production must necessarily be based on an assessment of the ability of magnesium to compete on a price basis, in this case with aluminum in automotive applications. It has been suggested earlier in this chapter that magnesium could be price competitive with aluminum based on an assessment of past and present trends in relative price. However, an assessment of the cost of producing magnesium by various techniques is required to quantify the competitive position of magnesium in automotive applications.

5.4.1 Historical Developments in the Production Economics of Magnesium

During World War II, magnesium production capacity was expanded rapidly by the Defense Plant Corporation at the request of the War Production Board. A total of thirteen magnesium plants were built in addition to nine aluminum plants. Magnesium production and consumption reached a peak during this period to which it is only now returning, Figure 5.4.1.1. Aluminum production exceeded that of magnesium by only 4 to 1 in the early 1940's versus the current 33 to 1 ratio.

Production data for the wartime magnesium and aluminum facilities were made available by the Defense Plant Corporation at the end of the war(6). The relative cost of producing magnesium and aluminum in 1945 in the more efficient of these government built plants is presented in Table 5.4.1.1. The most efficient government-built plant then in operation produced magnesium at a cost of 11.5 cents per pound. The most efficient government-built aluminum plant in existence at that time produced aluminum at only a slightly lower cost, 10.6 cents per pound(6). These production cost figures imply a pricing ratio of less than 1.1 to 1.0.

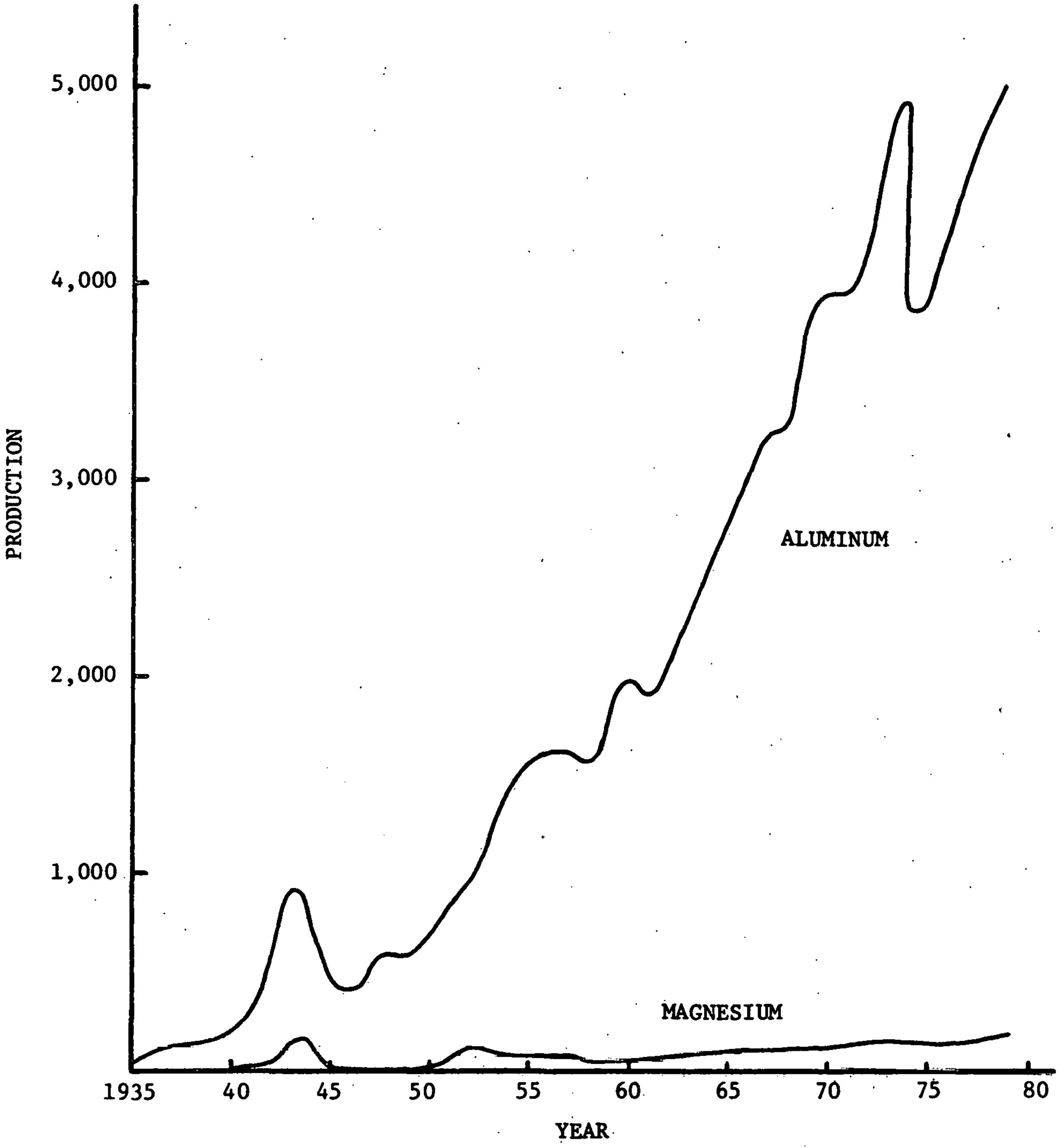


Figure 5.4.1.1: U.S. Production of Magnesium and Aluminum (X1000 tons).

TABLE 5.4.1.1

Production Data by Magnesium and Aluminum Facilities Built by the U.S. Government During World War II

	Magnesium Facilities				Aluminum Facilities			
	Velasco	Painesville	Las Vegas	Luckey*	Spokane	Troutdale	Jones Mills	Los Angeles
	(¢/lb)				(¢/lb)			
Raw Materials	1.1	5.2	4.4	9.5	5.6	5.8	4.7	5.7
Labor	3.1	1.8	3.8	1.9	1.0	1.3	1.0	1.6
Energy	1.8	5.2	2.5	2.4	1.8	1.9	4.0	4.3
Supplies, etc.	2.2	1.8	1.9	2.9	2.2	2.0	2.0	2.1
Direct Operating Cost	8.2	14.0	12.6	16.7	10.6	11.0	11.7	13.7
Overhead & Administration	1.9	1.0	3.3	1.0	-	-	-	-
Fees, Taxes, etc.	1.4	1.3	2.1	0.7	-	-	-	-
Total Cost: lowest single month	11.5	16.3	18.0	18.3				
lowest 3 month period	12.1	16.5	18.7	18.9				
lowest 9 month period					10.6	11.0	11.7	13.7
Average Overhead, Administration, Fees, Taxes, etc. for Mg Facilities					3.2	3.2	3.2	3.2
TOTALS:	12.1	16.5	18.7	18.9	13.8	14.2	14.9	16.9

*Ferrosilicon, all others electrolytic

At the close of World War II, magnesium production and use declined substantially, Figure 5.4.1.1, and all U.S. facilities were closed with the exception of Dow's plant in Texas. In contrast, the aluminum industry grew rapidly and some of the original wartime aluminum facilities, with modifications, are still in operation.

The magnesium industry, having remained relatively small, has not been able to match the amounts of capital devoted to research and development by the aluminum industry. Since current total magnesium production amounts to only 2 percent that of aluminum, it is not unreasonable to expect a corresponding level of research and development expenditure. Nevertheless, significant improvements have been made in magnesium production technology as relected by reduced total production energy requirements, Table 5.4.1.2, and as discussed in the previous two Chapters.

Over the past three decades, the energy requirement of the electrolytic portion of the magnesium process has declined by nearly 45 percent. This is roughly equivalent to the improvement in the energy efficiency of aluminum electrolytic cell technology over the same period(14). The parallelism in the improvement of the energy efficiency of these two processes is to be expected due to the similarity of the technology involved. This fact makes it even more difficult in technical terms to justify the recent divergence in the relative price of magnesium and aluminum, Figure 5.2.3.

5.4.2 The Economics of Current Magnesium Production Technology

In order to determine the economic viability of expanded magnesium use in the automotive sector and the potential of technical developments and innovations to modify future magnesium production costs, it is first necessary

Table 5.4.1.2

Energy Requirements for Magnesium Production

Process	Energy (KWH/Kg Mg)
Electrolysis and Thermal Reduction	
Dow: Old Cells(7)	21.3
Modified IG Cells(8)	15-18
Alcan: New Cells(8)	14
U.S.S.R.: Diaphragmless Cells(8)	13-15
Norsk Hydro: Old IG Cells	13-14
New Cells(10)	12-13
Bipolar Cells*	10
SOFREM: Magnetherm(11)	17.2
Cell/Furnace Feed Preparation	
Dow: Seawater/Dolomite(7)	14.4
NL: Solar Ponding(12)	16
Nalco: Solvent Extraction(13)+	5.0-8.4
Ferrosilicon Reductant(11)	11.7

*Projected

+Laboratory scale level of development

to quantify the capital and operating costs of current magnesium primary production processes.

Capital cost calculations for the DOW seawater process, modified IG Farbenindustrie process with Great Salt Lake solar ponding, and Magnetherm process are presented in Figure 5.4.2.1. These calculations are based on both currently available and historical capital cost data. The Chemical Engineering Plant Cost Index is used as the best available escalation factor to convert all of the available capital cost data to current 1980 dollars. Since the capital cost data correspond to a range of facilities with various levels of production capacity, the "six-tenths rule" technique has been used to generate the normalized functions presented in Figure 5.4.2.1. The slopes of these calculated log-log normalized capital/capacity curves do approximate the six-tenths rule. It should be noted that there are inherent error terms associated with six-tenth rule calculations and the use of capital cost escalation factors. Consequently, the curves presented in Figure 5.4.2.1 should be assigned a ±30 percent confidence interval.

At the lower levels of annual production capacity, the Magnetherm process appears to be the least capital intensive. For larger capacity facilities, the economies of scale associated with the Dow process make it the least capital intensive of the processes considered. The modified IG process is the most capital intensive over the range of capacities considered.

The operating costs for the three major domestic magnesium production technologies have been calculated, Figure 5.4.2.2, for greenfield facilities with the following geographic specifications:

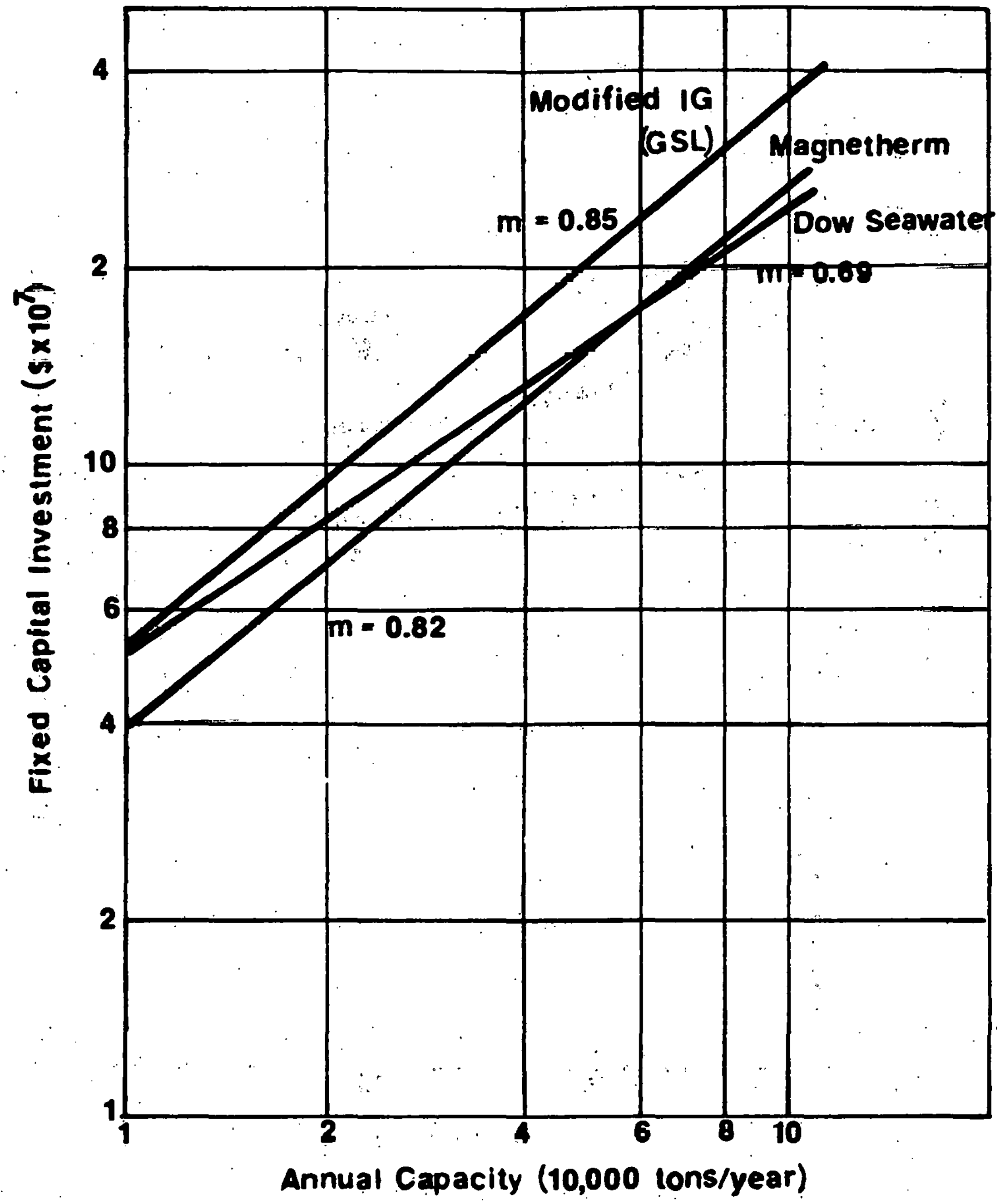


Figure 5.4.2.1: Estimated Capital Cost Requirements.

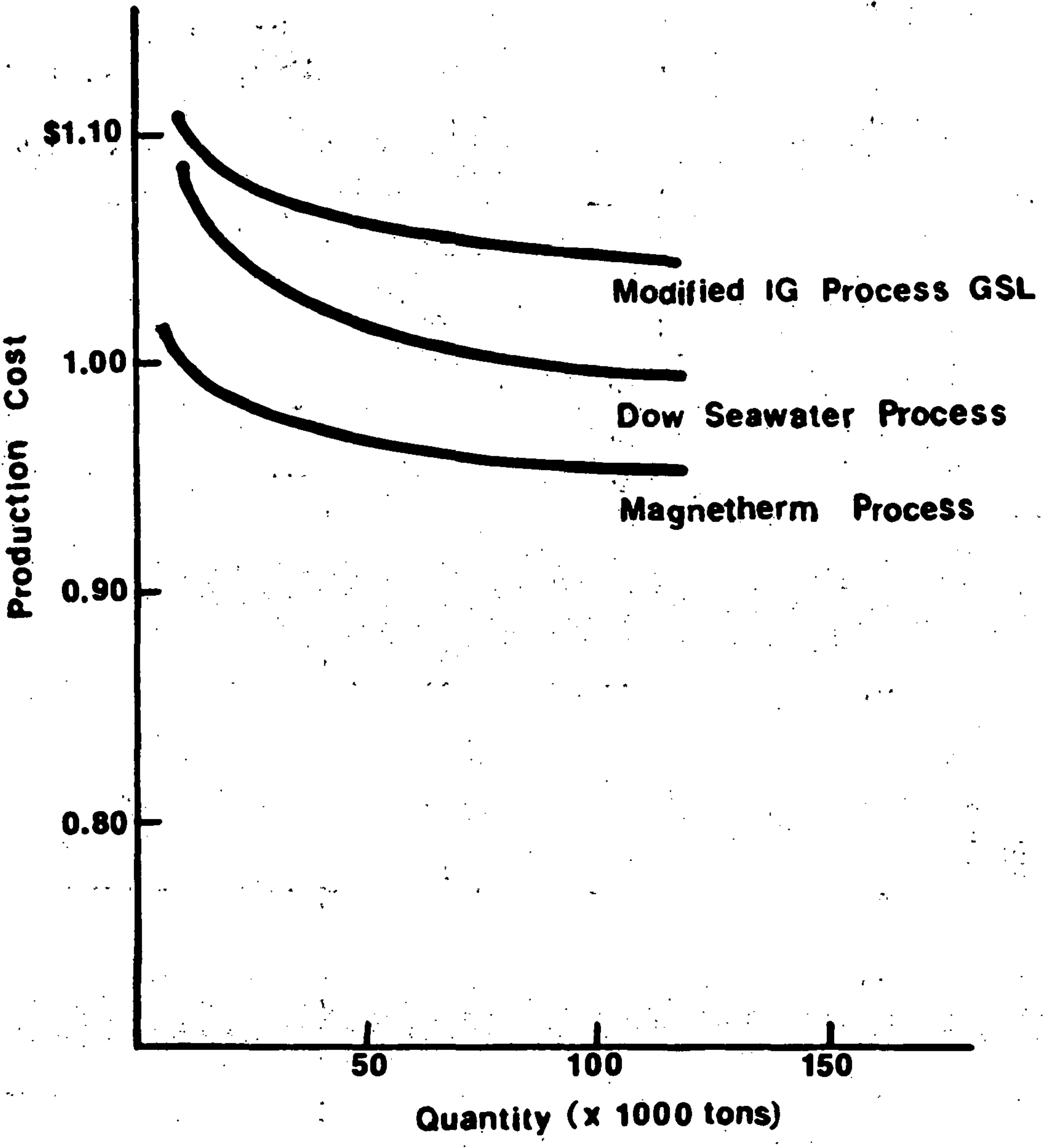


Figure 5.4.4.2: Product Cost Schedules.

1. Dow seawater process -- Texas,
2. IG Farbinindustrie process based on solar ponding -- Great Salt Lake, Utah, and
3. Magnetherm process -- Washington.

All of the production cost factor inputs, such as raw and operating materials, utilities, labor, overhead, by-product credits, taxes and insurance, and depreciation, are included in this calculation.

The curves presented in Figure 5.4.2.2 reflect the capital cost requirements presented in Figure 5.4.2.1 and therefore represent the total cost per unit of output for these processes at various levels of production capacity. By-product credits are assigned only to the Magnetherm process. Chlorine credits for the anhydrous modified IG process, while possible, are not included here because of potential chlorine marketing problems.

The calculated operating cost curves of Figure 5.4.2.2 indicate that domestic greenfield facilities based on currently available technologies are very cost competitive. The Magnetherm process is estimated to be the most cost effective while the modified IG process is the least cost effective. The hydrous Dow seawater process is estimated to be at a slight operating cost disadvantage compared with the Magnetherm process. However, it should be noted that these calculations are for greenfield facilities and not the actual facilities currently in operation. For instance the Dow facility in Texas, due to its age, would not have the full capital depreciation charge to contend with and would subsequently be much more economically competitive. It should also be noted that the geographic specifications made here for these processes may be suboptimal.

At the current magnesium price of $1.25 per pound, it is clear from Figure 5.4.2.2 that entry into magnesium production based on existing technology would result in a positive cash flow. For example, entry at a production capacity level of 50,000 tons per year would result in a pre-tax return on investment of roughly 20 to 30 percent. However, this return on investment is marginally sufficient to warrant entry into magnesium production geared towards the existing inelastic, non-structural market. Since penetration of the automotive light weight materials market will require a 10 percent or greater reduction in the current price of magnesium, Figure 5.3.2, the production economics of existing magnesium technologies preclude entry directed specifically towards penetration of the automotive market.

5.4.3 Future Magnesium Production Economics and the Automotive Market

Figure 5.4.2.2 implies that a new greenfield magnesium facility, based on currently available technology, would be economically viable in the current nonstructural market for magnesium. However, the profit margin available from such a facility is insufficient to allow for the 10 percent price reduction required to penetrate the automotive market. Consequently, a 10 percent increase in production efficiency based on process innovations or improvements with a corresponding reduction in the production cost of magnesium is required to make the automotive market available to magnesium on a competitive price basis.

The critical question concerning the future potential of magnesium in the elastic automotive market is whether a modest 10 percent or greater improvement in magnesium production efficiency is possible. This goal appears to be reasonable in light of recent developments. For example, Dow is currently engaged in a 10 year (1975 to 1985) energy conservation program aimed at reducing total energy requirements by 30 percent at their magnesium facility. At current energy prices, this will result in roughly a 10 percent reduction in production costs. In addition, Dow is also currently piloting a new electrolytic magnesium process which will further reduce total energy requirements by 20 percent(15). These two programs combined to provide the 10 percent productivity improvement necessary to compete effectively in the automotive market. However, the effect of the new technology on production efficiency will be diluted by the continued operation of the old technology. Consequently, penetration of the automotive market will be a slow evolutionary process throughout the 1980's, given this scenario.

On the other hand, new technologies have recently been proposed upon which new, more efficient facilities would be based. For example, a new high purity electrolytic cell feed preparation process has been proposed by Nalco Chemical Company which requires only half the energy of current technologies(13). Cell feed prepared in this way could increase the efficiency of existing cell technology and reduce total production cost.

The Nalco scenario is but one of several suggestions made in Chapters 3 and 4 for improving the production efficiency of electrolytic, metallothermic, and carbothermic magnesium production technologies. For example, suggestions have been made for converting current metallothermic technology from batch to continuous operation. This innovation would directly reduce operating costs by 30 percent by eliminating the current losses of magnesium to magnesium oxide. U.S. patents describing innovative carbothermic processes have also been discussed. These could lead to the reintroduction of the carbothermic processes which is inherently the most energy efficient of all the magnesium production technologies considered.

It is obvious that sufficient potential exists to improve the efficiency of magnesium production technologies by more than the 10 percent required to initiate penetration of the automotive market. However, if magnesium penetration of the automotive market is to occur rapidly, a research and development effort will be required to demonstrate the commercial viability of one or more of the suggested technical innovations. Following this, the growth potential of the automotive market will provide the financial incentive for a firm or firms to commercialize this process.

5.5 A FRAMEWORK FOR ANALYZING THE POTENTIAL FOR MAGNESIUM PENETRATION OF THE AUTOMOTIVE MARKET

A framework for analyzing the dynamics of intermaterial competition has been developed to evaluate the necessary conditions for and potential of magnesium penetration of the automotive market. This framework consists of an economic/engineering systems simulation model, the structure of which represents the three major determinants of automotive international competition:

1. the demand for automotive materials as influenced by general levels of economic activity and technological change within the automotive market,
2. the production capacity and availability of materials as determined by the supply-demand balance of competing materials, and

3. the desired market split of the automaker for materials as established by economic and technical feasibility.

It is expected that the simulation model will be useful in analyzing the substitution dynamics and associated demand for either two substitute materials in a specific fabricated form in a particular end use, or more generally for all substitute materials in any form for all applications within an end use sector.

The scope and structure of the simulation model is described in a current publication which is enclosed as Appendix I of this chapter. Work is continuing in this area.

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