



# Lowering of CO<sub>2</sub> Emission for Magnesium Production by Gossan-Zuliani Process

---

**PUBLIC**

A Report to:

Mr. Douglas Reeson  
Chairman and CEO  
Gossan Resources Limited  
404-171 Donald Street  
Winnipeg, Manitoba R3C 1M4

Submitted by:

Process Research ORTECH Inc.  
2350 Sheridan Park  
Mississauga, Ontario L5K 2T4

Date

Apr 20, 2012

- 1) This report is provided pursuant to an agreement between Process Research ORTECH Inc. and the addressee in respect of services provided to the addressee, and is subject to the terms of the agreement, and the limitations stated in the report.
- 2) This report is for the consideration of the addressee only, and may not be published or distributed without our written consent. Anyone other than the addressee who receives a copy of this report is advised that there are limitations concerning its contents which may require professional interpretation. Process Research ORTECH has no liability to anyone, other than its contractual obligations to the addressee, for any losses, expenses or damages occasioned by the use, distribution or circulation of this report.
- 3) Neither this report nor our name may be used in any way in connection with the sale, offer or advertisement of any article, process or service, the raising of capital or the making of any investment.
- 4) This report refers only to the particular samples, units, material, instrument, or other subject used and referred to in it, and is limited by the tests and/or analyses performed. Similar articles may not be of like quality, and other testing and/or analysis programs might be desirable and might give different results. The mention of commercial products, their source or their use in connection with material reported in this report is not to be construed as an actual or implied endorsement.
- 5) Apart from Process Research ORTECH's obligations to meet normal professional standards in performance of the agreement there is no representation, warranty, guarantee or other obligation of Process Research ORTECH or its employees arising out of this report. In particular, Process Research ORTECH makes no warranty or representation with respect to the usefulness of any information, apparatus, method or process disclosed in this report, or that the use of any information, apparatus, method or process disclosed in the report may not infringe privately owned rights.

## Table of Contents

1.0 Executive Summary .....	4
2.0 Magnesium Production Methods .....	6
2.1 Thermal Reduction with carbon, calcium or aluminum .....	6
2.2 Thermal Reduction with Silicon .....	7
2.2.1 Pidgeon Process .....	7
2.2.2 Magnetherm Process .....	8
2.3 Electrolytic Production of Magnesium .....	9
3.0 Recent Developments in Magnesium Production .....	9
3.1 Pidgeon Process in China .....	10
3.2 Zuliani Process .....	11
4.0 Comparison of Pidgeon Process in China and Gossan-Zuliani Process .....	12
4.1 Calcination of dolomite .....	13
4.2 Ferrosilicon production .....	13
4.3 Magnesium reduction .....	13
5.0 Material balance, heat balance and CO <sub>2</sub> emissions .....	14
5.1 Material Balance .....	14
5.1.1 Pidgeon Process in China .....	14
5.1.2 Gossan-Zuliani Process .....	15
5.1.3 Comparison of Pidgeon Process in China and Zuliani process .....	15
5.2 Heat balance .....	16
5.2.1 Pidgeon Process in China .....	16
5.2.2 Gossan-Zuliani process .....	16
5.2.3 Comparison of Pidgeon Process in China and Gossan-Zuliani Process .....	16
5.3 Carbon Dioxide Emissions .....	17
5.3.1 Pidgeon Process in China .....	18
5.3.2 Gossan-Zuliani Process .....	18
5.3.3 Comparison of Pidgeon Process in China and Gossan-Zuliani Process .....	18
6.0 Life Cycle Assessment Implications – CO <sub>2</sub> Emissions in Transport .....	20
6.1 STEP 1: Cradle to Entry Gate .....	20
6.2 Entry Gate to Exit Gate .....	22
6.3 Exit Gate to Grave .....	22
6.4 Overall Cradle to Grave Emissions .....	22
6.5 Cradle to Grave Benefits from the Use of Magnesium Produced with the Zuliani-Gossan Process	23
7.0 Conclusion .....	24
8.0 References .....	26

APPENDIX A- MASS BALANCES .....	28
APPENDIX B- HEAT BALANCES .....	31
APPENDIX C- CO <sub>2</sub> EMISSION CALCULATIONS.....	36
APPENDIX D- PROCESS FLOW DIAGRAM .....	38

## 1.0 Executive Summary

This report details the process efficiencies and environmental benefits of a new breakthrough magnesium primary production process (the “Zuliani Process”) being developed jointly by Dr. Douglas Zuliani and Gossan Resources Ltd. Gossan intends to produce magnesium metal with the highly efficient Zuliani Process using hydroelectricity, natural gas and its high quality dolomite resource located near Winnipeg in Manitoba, Canada. Importantly, the environmental benefits reported herein would be transferable to any geographic region employing the Zuliani Process with clean electricity and natural gas.

Magnesium is the eighth most abundant element in the Earth’s crust being naturally found in ores such as dolomite (MgCO<sub>3</sub>.CaCO<sub>3</sub>); magnesite (MgCO<sub>3</sub>); brucite (Mg(OH)<sub>2</sub>) and carnallite (MgCl<sub>3</sub>KCl.6H<sub>2</sub>O) [1]. Minerals containing magnesium are crucial to all life on earth; humans require about 200 mg of mineralogical magnesium every day [2].

In its metallic form, magnesium is employed in both nonstructural and structural applications.

Nonstructural uses include aluminum alloying, deoxidation and desulphurization of molten metals, as a graphite modifier in cast irons, as an ingredient in pyrotechnics and in an assorted number of other applications based on magnesium’s chemical properties.

As the world’s lightest structural metal, magnesium containing alloys are used extensively in many applications particularly in transportation and for portable electronic devices where magnesium imparts not only light weight but also excellent machinability, damping capacity, stiffness, corrosion resistance and electromagnetic shielding. Magnesium alloys exhibit the highest strength to weight and stiffness to weight ratios in many structural applications and typically provide weight savings of between 50-75% over conventional steel, 40-60% over high strength “light steel” and 20-35% over aluminum. In addition, magnesium alloys also demonstrate excellent castability, fabrication characteristics and dent resistance.

From an environmental and performance perspective, ultra-light magnesium components have the potential to significantly reduce vehicle weight which in turn has important implications for reducing emissions from combustion engines and increasing the range of electric vehicles.

In a comprehensive 2004 report, the United States Automotive Materials Partnership (“USAMP”) [17] determined that a total of 159 kg of magnesium could be incorporated into the average North American car which represents an increase of 154 kg over today’s average of 5 kg. USAMP estimated that a total weight savings of 227 kg could be realized by direct substitution weight savings of about 132 kg from replacing 226 kg of cast iron and steel and 59 kg of aluminum with 154 kg of magnesium. In addition, there will be secondary weight savings expected to be a further 95 kg as a result of vehicle redesign efficiencies arising from the addition of 154 kg of ultra-light magnesium parts. USAMP estimates that

the net result would be a 15% reduction in total vehicle weight and a corresponding 8% improvement in fuel efficiency.

Today, more than 77% of the world's magnesium is produced in China using the very energy intensive Pidgeon thermal reduction process [3] that was originally developed in 1944. As a result of China's extensive use of fossil fuels, Chinese magnesium production has raised serious environmental concerns [4].

The Global Warming Potential (GWP) for Chinese magnesium has been reported as 43.3 kg CO<sub>2</sub> per kg of Mg ingot [11]. By comparison, the average GWP for aluminum ingot is 12.7 kg CO<sub>2</sub> per kg of Al ingot [16] or almost 3.5 times lower.

This report develops the mass & energy balance relationships needed to determine the GWP for magnesium produced by thermal reduction of calcined dolomite with ferro-silicon (FeSi). The current mass & energy balance method was benchmarked against previously published data to ensure correctness; the current study determined the GWP for Chinese magnesium ingot produced with the Pidgeon Process using coal as the primary energy source is 42.0 kg CO<sub>2</sub> per kg of Mg which agrees to within 3% of the previously published GWP of 43.3 [11].

These mass & energy balance relationships were subsequently used to determine that the GWP of the Zuliani Process is 9.1 kg CO<sub>2</sub> per kg of Mg ingot for this highly efficient process when employing natural gas to calcine dolomite and hydroelectricity to reduce the calcined dolomite with FeSi also produced with hydroelectricity. The 9.1 GWP of the Zuliani Process is 4.8 times lower than the GWP for Chinese Mg ingot and 1.4 times lower than the average GWP for Al ingot.

As explained in section 6 of this report, D'Errico et al. [9, 14] have developed the methodology for determining a Life Cycle Assessment (LCA) when using magnesium alloy parts in transportation. Even when assuming the most efficient SF<sub>6</sub> free near net shape casting technology for Mg parts manufacture (entry gate to exit gate GWP of 2 kg CO<sub>2</sub> per kg Mg), the GWP for parts produced from Chinese magnesium would be 45.3 kg CO<sub>2</sub> per kg. A modern fuel efficient car incorporating weight savings of 227 kg from the addition of 154 kg of parts manufactured with Chinese Mg would have to travel almost 284,000 km before the additional "CO<sub>2</sub> generated" by the production of parts made from Chinese magnesium breaks-even with the "CO<sub>2</sub> saved" by improved fuel efficiency resulting from the reduced vehicle weight. As such, it is obvious that in spite of the significant weight and fuel saving opportunities determined in the USAMP study, the widespread use of parts manufactured from Chinese magnesium is not environmentally favorable from a total life cycle perspective.

Importantly, the resulting LCA for parts made with magnesium produced by the clean Zuliani Process shows that the mileage at which the additional GHG generated from magnesium part production will break-even with the GHG saved from the reduced vehicle weight is just over 69,500 km which would

make magnesium the most environmentally attractive weight-saving material. Based on a Life Cycle Analysis, substitution of cast iron, steel and aluminum with Zuliani process magnesium, at levels proposed (154kg) in the 2004 USAMP study, can reduce average midsize car emissions by almost 7% over the car's life expectancy of 200,000 km.

## 2.0 Magnesium Production Methods

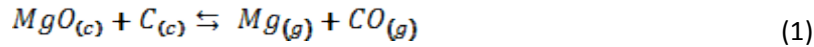
Commercially magnesium production processes can be classified into two main groups; electrolysis and thermal reduction.

Magnesium electrolysis is a large scale, continuous process employing electricity to reduce magnesium chloride containing molten salt to molten crude magnesium metal for subsequent refining and casting into commercial forms. Electrolytic process technology is generally complex involving many independent process steps. Very specialized electrolytic cell technology together with high purity anhydrous MgCl or equivalent is necessary to achieve acceptable electrical efficiency and energy costs. While generalized methods have been disclosed, the specific process technology details are not routine or widely known. Because of process complexity, capital costs for a modern electrolytic magnesium plant can approach or exceed \$1 billion. Achieving an adequate return on capital requires plant production capacities of the order of 50,000 tpa or higher. Electrolysis also faces increasingly stringent standards associated with chlorine emissions and related by-products.

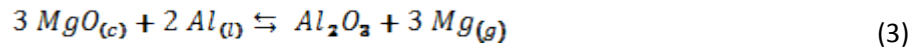
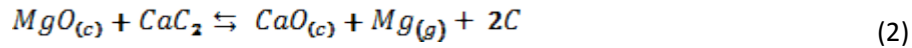
While magnesium oxide can in theory be reduced by carbon, calcium and aluminum, for technical and operating cost reasons, commercial thermal reduction processes rely almost exclusively on ferro-silicon reduction of calcined dolomite ore. Appropriate mixtures of calcined dolomite and ferro-silicon are heated in either solid or molten state under vacuum to produce magnesium vapor which condenses into solid, crude magnesium for subsequent melting, refining and casting into ingots/commercial products. In general, commercial thermal technology is a batch process that suffers from being labor and maintenance intensive, from poor raw material utilization efficiencies, from high energy consumption, from additional costs & yield losses associated with the crude magnesium melting step and from environmental concerns due to high by-product waste and GHG emissions. However, because of their relative simplicity and lower capital cost, thermal plants can be built in much smaller increments of the order of 10,000 tpa or less.

### 2.1 Thermal Reduction with carbon, calcium or aluminum

As one of the most stable oxides, high temperature (~1800 °C) is required to reduce magnesium oxide with carbon (equation 1). By applying vacuum distillation the reduction temperature can be lowered as the reaction products will become favored. However it is difficult to prevent the backward reaction of magnesium vapor with carbon monoxide and therefore this method has not been used to produce magnesium commercially [1].



Other reductants such as CaC<sub>2</sub> and Al (equation 2 & 3) have been used to reduce MgO at 1200 °C under vacuum conditions. Although MgO reduction with CaC<sub>2</sub> and Al work technically, neither is used commercially due to economic reasons.



## 2.2 Thermal Reduction with Silicon

Unlike carbon, calcium and aluminum, reduction of magnesium oxide in the form of calcined dolomite by silicon usually contained in a ferro-silicon alloy is a commercially viable practice. Two commercial processes have been developed, solid state silicothermic reduction of calcined dolomite at about 1200°C under vacuum, or, molten state silicothermic reduction of MgO contained in a liquid CaO, MgO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> melt at about 1500°C under vacuum.

### 2.2.1 Pidgeon Process

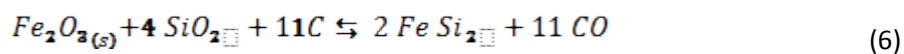
Pidgeon and Alexander [10] in 1944 developed a solid state process that made it commercially feasible to produce magnesium by thermal reduction of calcined dolomite ore often referred to as dolime (CaO.MgO). In this process, MgO contained in the dolime is reduced according to equation 4 by silicon contained in a ferro-silicon alloy, under vacuum.



Dolomite calcination, reaction (5) is carried out to produce dolime by removal of carbon dioxide from the dolomite ore. Calcination is normally carried out at 1200 °C [5].



Ferro-silicon is produced by reactions (6) & (7) usually in a submerged arc electric furnace at about 1723°C.



Ferro-silicon and calcined dolomite are first ground in a hammer mill or the like, mixed together in the appropriate amounts according to the stoichiometry of reaction (4) and made into briquettes to ensure intimate physical contact between the raw materials which is necessary for the solid state reduction reaction. The briquettes are charged into high alloy retorts which are nominally 3 meters in length and

25-30 cm in diameter. The briquettes are held under vacuum at about 1200°C for about 8 to 9 hours. It has been postulated that the reduction process takes place in two distinct stages, initially between calcium oxide and ferrosilicon to produce a liquid Ca-Si-Fe alloy, which spreads throughout the briquette to form a metallic network. This mildly exothermic reaction takes place rapidly at around 1000°C. Magnesium vapor is subsequently liberated from MgO by reduction by the Ca-Si-Fe alloy [1]. Pressure builds up inside the sealed retort reactor, which slows the rate of the reaction since the reaction is endothermic. Thus, the rate at which magnesium vapor can escape dictates the reaction rate.

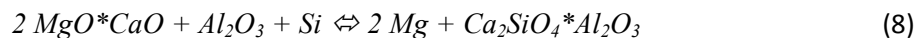
The resulting magnesium vapor is condensed in a water cooled section of the retort. After the prescribed time, the vacuum seal is broken, the retort is opened and the crude solid magnesium condensate (referred to as a crown) is removed along with the spent briquettes. Prior to commercial sale, the solid magnesium crowns must be melted, refined and cast into ingots which, adds further energy consumption, cost and yield losses.

Today, the Pidgeon process is used in China to produce approximately 80% of the world's magnesium metal.

A variant of the Pidgeon process was originally developed by Bolzano in Italy and is now used by RIMA in Brazil to produce about 2-3% of the world's magnesium. While the scale of the Bolzano process reduction furnace is somewhat larger than the Pidgeon process retort, this solid state process still requires a vacuum to produce a solid crude Mg condensate with raw materials utilization efficiencies similar to the Pidgeon process. As with the Pidgeon process, the solid crude magnesium must be melted and refined prior to casting into commercially saleable forms.

### 2.2.2 Magnetherm Process

The molten state Magnetherm process also uses ferro-silicon to reduce magnesium oxide to produce magnesium [6]. The process is however carried out at about 1500 °C and the dolime is maintained in molten form by adding alumina to decrease the melting point of the oxide reactant [3].



The Magnetherm reaction produces Mg vapour and a molten discard slag which contains significant quantities of unreacted MgO and FeSi . Like the Pidgeon Process, the Magnetherm process requires a vacuum and condenses the Mg vapour as a solid which requires melting before refining and ingot casting.

While the scale of the Magnetherm process is substantially larger than the solid state processes, raw material utilization efficiencies are not significantly improved. While the Magnetherm process was previously used on a large scale by Pechiney in France and Alcoa in the USA as well as in a few other



smaller facilities worldwide, all Magnetherm facilities have now been shut down and the process is no longer in commercial use.

### 2.3 Electrolytic Production of Magnesium

The Electrolytic process is based on fused salt electrolysis of anhydrous magnesium chloride. Several methods exist to produce suitable magnesium chloride feedstock including the salt water process (Dow Chemical), dehydration of brines (US Magnesium), the use of carnallite (Russian & Dead Sea) and the conversion of magnesium hydroxide (Norsk Hydro) where the mineral magnesite is leached with HCl to produce anhydrous MgCl<sub>2</sub> as per reaction (9).



In general, electrolytic processes use electricity to reduce high purity anhydrous magnesium chloride to produce molten magnesium metal according to equation (10).



In spite of being highly capital cost intensive, electrolytic technology has the advantage of being able to produce molten, crude magnesium continuously on a very large scale thereby avoiding the additional energy, operating cost and yield loss associated with the melting of solid magnesium crowns and the process stops and associated lost productivity incurred with the batch thermal processes.

Prior to 1990, electrolysis was by far the dominant method for producing magnesium metal with large scale facilities being operated by Dow Chemical, Norsk Hydro, US Magnesium and Dead Sea Magnesium. However, due to the sharp decline in magnesium prices resulting from the widespread deployment of Pidgeon process technology in China over the last 20 years, today only US Magnesium, Dead Sea Magnesium and a few smaller former Soviet based facilities remain in operation producing somewhat less than about 20% of the world's magnesium supply.

### 3.0 Recent Developments in Magnesium Production

Since the early 1990's, China has seen rapid growth in magnesium production. While the production of magnesium in China was virtually zero before 1990, by 2005 production had reached 816,000 t corresponding to 70% of global output [8], increasing further to 77 % of global output by 2007 [3]. Today, Chinese plants use the Pidgeon process almost exclusively to produce approximately 80% of the world's magnesium.

The generally low raw materials utilization efficiencies with the Pidgeon process together with the widespread use of coal and in some instances coke oven gas used to provide process energy has raised serious environmental concerns with Chinese magnesium production. Recently, Dr. Douglas J. Zuliani in

cooperation with Gossan Resources has developed a new thermal process for the production of magnesium and is currently in the process of commercializing this process.

### 3.1 Pidgeon Process in China

China produces essentially 80% of the world's magnesium using the Pidgeon process, which was invented by Pidgeon and Alexander in the 1940s in Canada. The Chinese variation of the Pidgeon process starts with the mining and transportation of dolomite ore and coal. Dolomite contains mainly CaCO<sub>3</sub> (58%) and MgCO<sub>3</sub> (39%). The dolomite is first calcined to produce dolime, which is a mineralogical mixture of magnesium oxide and calcium oxide. Carbon dioxide is released during the calcination process. This process is energy intensive, and in China coal is most often used as an energy source for the calcination reaction operated at 1200 °C. The dolime is subsequently ground in a hammer mill and screened to the required mesh size.

Ferrosilicon is the reductant used in the Pidgeon process. A large majority of the world's ferrosilicon is produced and sourced in China using coal generated electricity. Ferrosilicon is crushed and ground as finely as required using secondary grinders [2].

The next step is to mix and briquette the dolime and ferrosilicon in the correct proportions. A small quantity of calcium fluoride is usually added as a catalyst and the mixture of dolime, ferrosilicon and calcium fluoride is briquetted before being transferred to the next step in the process, which is magnesium reduction. Briquetting requires a much smaller amount of energy compared to other steps in the process.

In China the energy for the magnesium reduction process step is most often supplied by burning coal in one form or another. During the reduction process, the magnesium vapor is released and solid Ca<sub>2</sub>SiO<sub>4</sub> slag is formed which is usually discarded as a reaction by-product waste. The energy efficiency for the process is only about 12% [7]. The reduction reaction is carried inside small scale, high alloy retorts under vacuum conditions required to make the reaction thermodynamically favorable. The magnesium vapor is condensed in a water cooled end of the retort and recovered as solid crude magnesium "crowns", which are subsequently melted, refined and cast as magnesium ingot. Sulfur or other chemicals such as SF<sub>6</sub> are added over the exposed molten metal surface to prevent molten magnesium from oxidizing. The process steps are shown in Figure 1.

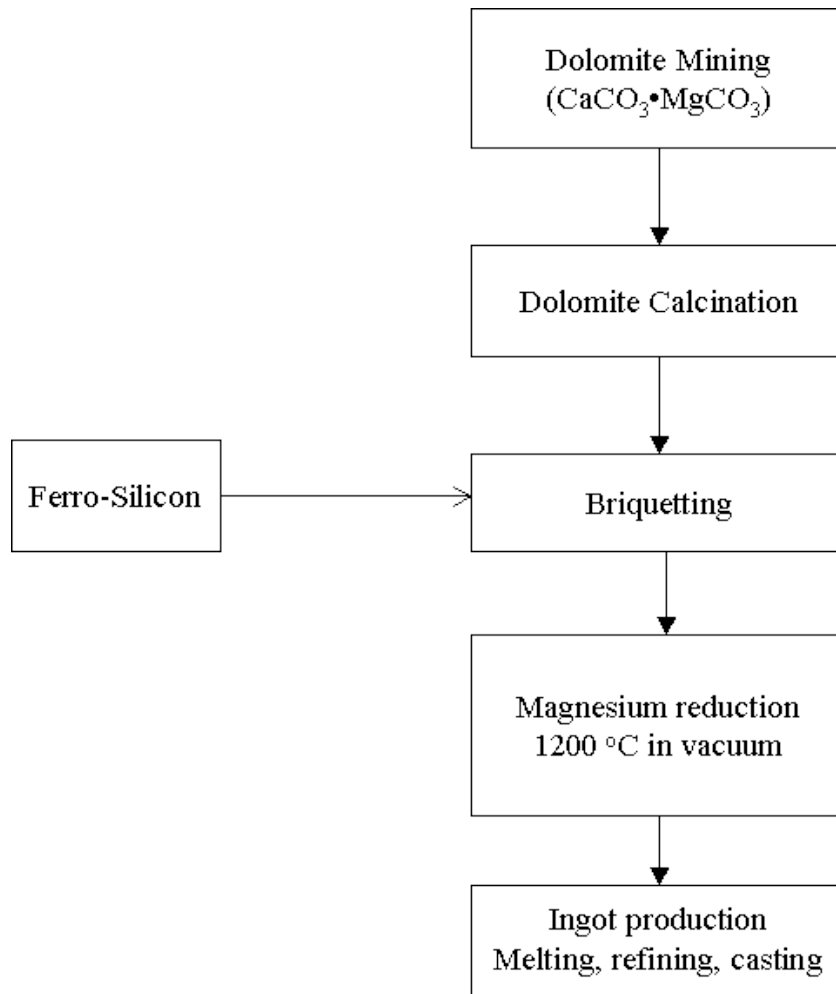


Figure 1: Pidgeon Process in China Flow Diagram

### 3.2 Zuliani Process

Gossan Resources is currently in the process of investigating a new process proposed by Dr. Douglas J. Zuliani – the intent is to commercialize the technology to produce magnesium metal in Manitoba Canada using local high purity dolomite and clean hydroelectricity and natural gas. Specific features of the Zuliani Process are currently held as a trade secret and are protected under confidentiality agreement. The process is an enhancement of the Magnetherm process and uses a molten melt at higher temperatures ( $\geq 1550^{\circ}\text{C}$ ) to produce magnesium vapor at atmospheric pressures for condensation as molten magnesium which is subsequently refined and cast into saleable product. The generalized process steps are shown in Figure 2.

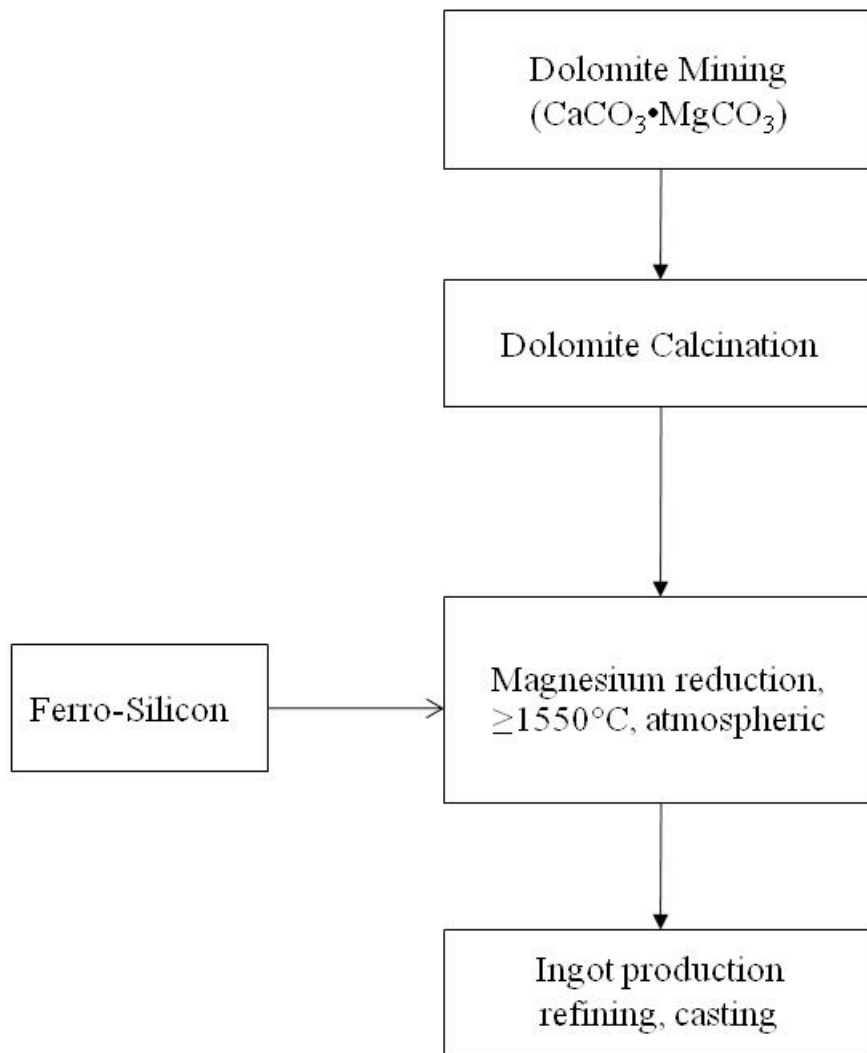


Figure 2: Zuliani Process Flow Diagram

#### 4.0 Comparison of Pidgeon Process in China and Gossan-Zuliani Process

The process efficiencies and the total direct plus indirect GHG emissions comparison reported in the following sections are based on;

- Pidgeon Process; because about 80% of the world’s magnesium is produced in China with the Pidgeon process, it was assumed to be the baseline case for magnesium metal production. This report utilizes recently published data on Chinese production practices [7], and,
- Zuliani Process; the results of FactSage thermodynamic modeling by Professor Pelton at Ecole Polytechnique, Montreal are taken together with independent experimental data from tests conducted by Process Research ORTECH. The GHG calculations are specific to Gossan’s proposed

Manitoba facility however they remain valid for any facility location using high grade dolomite, electric power generated from clean sources (hydro, nuclear or renewable) and natural gas for dolomite calcination.

#### **4.1 Calcination of dolomite**

Both process routes require calcination of dolomite however the Zuliani Process will require a less calcined dolomite for the same amount of magnesium metal produced due to a higher magnesium reduction efficiency than with the Pidgeon Process in China. In addition the Pidgeon Process in China uses coal-based heating for calcination of dolomite, whereas Gossan Resources will use natural gas which is abundantly available in Manitoba. This will result in lower CO<sub>2</sub> generation, since burning of natural gas produces less CO<sub>2</sub> compared to burning of coal to realize an equivalent amount of energy.

#### **4.2 Ferrosilicon production**

For the ferrosilicon production step, the Pidgeon Process in China uses electric power that is generated by burning coal. Rather than purchase ferrosilicon from China, Gossan Resources intends to produce ferrosilicon in Manitoba using abundantly available hydroelectric power. Thus indirect CO<sub>2</sub> will not be generated for the power used in the Zuliani Process when utilizing clean electricity, whereas there will be CO<sub>2</sub> generated for the energy required to produce FeSi in China.

#### **4.3 Magnesium reduction**

For the magnesium reduction process, the Pidgeon Process in China uses coal based heating for the reduction of dolime, while Gossan Resources will use Manitoba hydroelectric power thereby generating no additional indirect CO<sub>2</sub> from the reduction process. To achieve increased magnesium recovery, atmospheric Mg pressures and molten Mg condensation, the Zuliani Process reduction reaction occurs at approximately 1600 °C rather than at 1200 °C under vacuum as required for the Pidgeon process. Even though the energy requirements for the higher temperature reaction will be greater than the Pidgeon Process in China, the net energy input will be lower due to high utilization efficiency of hydroelectric power compared to coal based heating.

A comparison of Pidgeon Process in China and Gossan-Zuliani Process is shown in Table 1.

**Table 1: Comparison of Pidgeon Process in China and Gossan-Zuliani Process**

	Pidgeon Process in China	Gossan-Zuliani Process
Calcination of dolomite	Coal used for heating	Natural Gas used for heating  Less dolomite calcined per unit of Mg production due to higher process efficiency
Ferrosilicon production	Coal generated electricity	Hydro-electricity  Less ferrosilicon needed per unit of Mg production due to higher process efficiency
Magnesium reduction	Coal used for heating to produce solid crude Mg crowns	Hydro-electricity used to produce molten crude Mg metal, no additional CO <sub>2</sub> generated.
Magnesium ingot casting	Coal generated electricity used to melt solid crowns for refining & ingot casting	Hydro-electricity used to maintain molten metal temperatures during refining & ingot casting

## 5.0 Material balance, heat balance and CO<sub>2</sub> emissions

### 5.1 Material Balance

The basis of the mass balance is the production of 1 kg of magnesium ingot. The composition of ferrosilicon used for reduction is assumed to be 75% silicon and 25% iron, which is the commercial grade of ferrosilicon produced mainly for the steel industry.

#### 5.1.1 Pidgeon Process in China

The Pidgeon Process in China uses dolomite, which has 8% contaminants [7].

For the Pidgeon Process in China the reaction efficiency used for these calculations (% of dolime reacted) was 85.3% [7]. Dolime was the limiting reactant with the briquette mixture containing a stoichiometric excess of ferrosilicon. Unreacted FeSi remains in the discarded reaction by-product

dicalcium silicate that is at present sent to a waste dump and not recovered. The overall recovery of magnesium ingot from Pidgeon Process in China after reduction and melting losses is 71.5% from the dolomite and 74% from dolime.

### 5.1.2 Gossan-Zuliani Process

For the Zuliani Process, Gossan Resources provided a sample of dolime with specified compositions. Gossan Resources uses high grade dolomite, containing only 1.6% impurities. The amount of dolomite was calculated based on 1 kg of magnesium ingot produced. The reaction temperature is assumed to be 1600°C. For calculating the amount of magnesium produced, it has been assumed that magnesium is produced mainly by the reduction of magnesium oxide by silicon; however a small amount of magnesium is also produced by the reduction of magnesium oxide by aluminum, which is always present in commercial ferrosilicon. The overall recovery of magnesium was determined to be 92.9% from bench scale experiments performed at Process Research ORTECH which is in excellent agreement with the 92.3% predicted by Pelton’s FactSage thermodynamic modeling. These results will need to be proven on a larger scale to determine if they can be achieved in commercial production.

### 5.1.3 Comparison of Pidgeon Process in China and Zuliani process

Table 2 shows the comparison of material balances for Pidgeon Process in China and Zuliani Process. Detailed calculations are shown in Appendix A. The overall recovery of magnesium from dolime for the Zuliani Process was calculated to be 90.4 % compared to 74.0 % for Pidgeon Process in China. The amounts of dolomite and ferrosilicon used are 17 % and 29 % lower respectively compared to the Pidgeon Process in China. A by-product of the Zuliani Process is residual ferrosilicon alloy, which can easily be recovered because of the process reactor design and sold as a commercial by-product.

**Table 2: Material Balance Comparison kg per kg Mg Ingot**

	Mg Ingot Recovery from dolime (%)	Dolomite Used (kg)	Dolime Used (kg)	FeSi Consumed by Reduction Reaction (kg)
Zuliani Process in Manitoba	90.40	9.67	4.55	0.85
Pidgeon Process China	73.96	11.6	5.36	1.19

## 5.2 Heat balance

During the production of magnesium, heat energy is required for three major process steps; dolomite calcination, ferrosilicon production and magnesium reduction. The dolomite calcination is carried out at 1200 °C. The reaction is highly endothermic.

### 5.2.1 Pidgeon Process in China

For calcination, Pidgeon Process in China uses coal as a heating source and the energy utilization efficiency is reported as 63.6 % [7], which results in 12,541 kcal of energy needed per kg of Mg produced.

For the ferrosilicon production stage, the heat required for Pidgeon Process in China is 6,811 kcal/kg of Mg. China uses coal-generated electricity for ferrosilicon production, and the energy utilization efficiency is calculated to be 42% [7], resulting in energy requirement of 16,352 kcal/kg Mg ingot produced.

For the magnesium reduction, the energy requirement for Pidgeon Process in China is 4561 kcal/kg of Mg. Since the Pidgeon Process in China uses heat generated by burning coal, which has an energy utilization efficiency of only 12% [7], the energy required is 43,000 kcal/kg Mg Ingot produced.

### 5.2.2 Gossan-Zuliani process

Gossan Resources will use natural gas to supply the heat for calcination and the assuming an efficiency of 63.6%, the energy required will be 10,517 kcal/kg of Mg.

For the ferrosilicon production stage, the energy required for Gossan-Zuliani process is 4,865 kcal/kg of Mg. Gossan Resources will use hydroelectric power and assuming energy utilization efficiency of 42%, the required energy will be 11,583 kcal/kg Mg ingot produced.

For the magnesium reduction, the energy requirements for Gossan-Zuliani process is 4,622 kcal/kg Mg. Gossan-Zuliani process will use hydroelectric power and assuming the energy utilization efficiency of 25% the required energy will be 18,488 kcal/kg Mg Ingot produced.

### 5.2.3 Comparison of Pidgeon Process in China and Gossan-Zuliani Process

Heat required for the calcination is lower for the Gossan-Zuliani Process compared to Pidgeon Process in China. The energy required is 12,541 and 10,517 kcal/kg of Mg for the Pidgeon process in China and Gossan-Zuliani Process respectively. For the ferrosilicon production stage, the energy required for Pidgeon Process in China and Gossan-Zuliani process are 16,352 kcal and 11,583 kcal respectively per kg Mg produced. The difference in the requirements for both processes is due to smaller amounts of



dolime and ferrosilicon needed to produce the same amount of magnesium with the more efficient Zuliani Process. The use of coal-generated electricity for ferrosilicon production in China, potentially has a higher energy loss but this was not taken into account in the calculations.

For the magnesium reduction, reaction conditions are significantly different in both processes. After taking into account the difference in energy utilization efficiency, the energy requirements are 43,000 kcal and 18,488 kcal per kg Mg ingot produced respectively for Pidgeon Process in China and Gossan-Zuliani process.

Table 3 shows the comparison of heat balance for both processes. Detailed calculations are shown in Appendix B.

**Table 3: Heat Balance Comparison**

Reactions	Dolomite Calcination		FerroSilicon Production		Magnesium Reduction	
	Pidgeon China	Zuliani Canada	Pidgeon China	Zuliani Canada	Pidgeon China	Zuliani Canada
Heating Method	Coal	Natural Gas	Coal	Hydro	Coal	Hydro
Temperature (°C)	1200	1200	1723	1723	1200	1600
Heat required for reaction (kcal/kg Mg ingot Produced)	8026	6688	6811	4865	4561	4622
Heat Input (kcal/kg Mg ingot Produced)	12541	10517	16352	11583	43000	18488
Energy Efficiency (%)	64	64	42	42	12	25

### 5.3 Carbon Dioxide Emissions

Generation of carbon dioxide is an environmental issue as carbon dioxide is a major green house gas responsible for global warming. Carbon dioxide is produced due to the decomposition of dolomite during calcination. Other sources of carbon dioxide during magnesium production are burning of coal or natural gas to supply the heat needed for process steps.

### 5.3.1 Pidgeon Process in China

Pidgeon process in China process uses coal based heating for dolomite calcination and magnesium reduction and coal generated electricity for ferrosilicon production. The total amount of carbon dioxide generated during dolomite calcination for the Pidgeon Process in China is 10.1 kg CO<sub>2</sub>/kg of Mg.

For ferrosilicon reduction step, Pidgeon Process in China produces 14.7 kg CO<sub>2</sub>/kg of Mg.

For the magnesium reduction step, Pidgeon Process in China produces 15.9 kg CO<sub>2</sub>/kg of Mg.

### 5.3.2 Gossan-Zuliani Process

Gossan-Zuliani process will use hydroelectric power for ferrosilicon production and magnesium reduction and natural gas for dolomite calcination. The total amount of carbon dioxide generated during dolomite calcination process for the Gossan-Zuliani process is 6.6 kg CO<sub>2</sub>/kg of Mg.

For ferrosilicon reduction step, the Gossan-Zuliani process will produce 2.2 kg CO<sub>2</sub>/kg of Mg, which will be generated from the reaction.

For the magnesium reduction step, the Gossan-Zuliani process will produce no CO<sub>2</sub> emission, since hydroelectric power is used.

### 5.3.3 Comparison of Pidgeon Process in China and Gossan-Zuliani Process

Gossan-Zuliani process produces lesser amount of carbon dioxide for the following reasons:

- The Zuliani process raw materials utilization efficiencies are higher due to more efficient use of dolime and FeSi compared to the Pidgeon process in China
- Natural gas is more energy efficient than coal, a lower amount of natural gas is required for producing the same amount of energy required by coal. Furthermore, natural gas produces 45% less carbon dioxide than burning coal [7]. The total amount of carbon dioxide generated during dolomite calcination reaction for the Pidgeon process in China and Gossan-Zuliani process are 10.1 and 6.6 kg CO<sub>2</sub>/kg of Mg respectively.
- For ferrosilicon reduction reaction, Pidgeon Process in China emits 14.7 kg CO<sub>2</sub>/kg of Mg, whereas the Gossan-Zuliani process has no emissions from hydroelectric power, but some CO<sub>2</sub> is released from the reaction, which amounts to 2.2 kg CO<sub>2</sub>/kg of Mg.
- For the magnesium reduction reaction, Pidgeon Process in China emits 15.9 kg CO<sub>2</sub>/kg of Mg, whereas the Gossan-Zuliani process has no emissions since hydroelectric power is used.

Table 4 shows the comparison of heat balance for both processes. The table also includes CO<sub>2</sub> generated during dolomite mining, briquetting and ingot production steps [7], however, their contributions are relatively smaller compared to dolomite calcination, ferrosilicon production and magnesium reduction steps. Detailed calculations are shown in Appendix C.

**Table 4: CO<sub>2</sub> emissions comparison**

Production stages	Pidgeon process in China CO <sub>2</sub> Emissions (kg/kg of Mg Ingot)	Gossan-Zuliani CO <sub>2</sub> Emissions (kg/kg of Mg Ingot)
Dolomite Mining	0.3	0.3
Dolomite Calcination	10.1	6.6
Ferrosilicon Production	14.7	2.2
Briquette Production	0.2	0
Magnesium Reduction	15.9	0
Magnesium Ingot production	0.7	0
Total	42.0	9.1

Table 5 shows the comparison of the CO<sub>2</sub> emissions in different countries, where magnesium is produced [9]. In comparison, Gossan Zuliani process will generate 9.1kg of CO<sub>2</sub> per kg of Mg ingot assuming ~90 % process efficiency. Appendix D shows the process flow diagrams of Pidgeon Process in China and Gossan-Zuliani process with the heat balance and CO<sub>2</sub> emission for each stage of processing.

**Table 5: Worldwide Magnesium CO<sub>2</sub> Emissions Comparison [9]**

Magnesium Production in the World	Primary Mg Production and Alloy Making CO <sub>2</sub> emissions (kg/kg of Mg Ingot)
Pidgeon Process in China	43.3
Norsk Hydro Magnesium (Canada)	16.1
AM (Australia)	27.93
Bolzano (Brazil)	13.80
Magnetherm (France)	17.60

## 6.0 Life Cycle Assessment Implications – CO<sub>2</sub> Emissions in Transport

Depending on the nature of the application, magnesium provides weight savings of between about 50-75% over conventional steel, 40-60% over high strength “light steel” and 20-35% over aluminum. As such, magnesium can play an important role in reducing vehicle weight and emissions while improving the range and performance of internal combustion, hybrid and electric vehicles.

Total Direct plus Indirect kg CO<sub>2</sub> <sub>equiv</sub> has been adopted as a measure of the Global Warming Potential (“GWP”) of various materials.

Life Cycle Assessment (“LCA”) determines the GWP for any Material from production through fabrication to end of use. For metals such as magnesium and aluminum the LCA is broken into three steps:

STEP 1: Cradle to Entry Gate – raw material extraction, smelting, refining & ingot casting

STEP 2: Entry Gate to Exit Gate – product manufacture such as casting, machining & finishing

STEP 3: Exit Gate to Grave – product use, recycling & disposal

### 6.1 STEP 1: Cradle to Entry Gate

Table 6 summarizes the STEP 1 Cradle to Entry Gate GWP for magnesium ingot produced by the various processes methods. By comparison the world average STEP 1 GWP for aluminum ingot is 12.7 kg CO<sub>2</sub>/kg [16] and is highly regionally dependent; 9.8 in North America, 11.0 in Europe and 24.7 in China.

**Table 6: Magnesium Ingot Production Process CO<sub>2</sub> Emissions Comparison**

Magnesium Production Process		STEP 1 Cradle to Entry Gate - GWP (kg CO <sub>2</sub> /kg Mg Ingot)	Reference
THERMAL	Zuliani (Canada)	9.1	present
	Bolzano (Brazil)	13.80	3
	Magnetherm (France)	17.60	3
	Pidgeon (China)	42.0 - 43.3	present, 11
ELECTROLYSIS	Norsk Hydro (Canada)	16.1	11
	AM (Australia)	27.93	12

From Table 6 the average STEP 1 GWP for electrolytic production is about 21 kg CO<sub>2</sub> equiv per kg Mg - Norsk Hydro Canada which is currently shut down employed hydro electricity generated in Quebec and can be considered representative of about the lowest CO<sub>2</sub> emissions potential for electrolytic magnesium.

In evaluating the thermal processes shown in Table 6, clearly the Pidgeon Process as practiced in China is not environmentally competitive particularly compared to the Bolzano Process as practiced in Brazil.

However, it should be noted that the Bolzano Process as practiced by RIMA in Brazil **[13]** is not materially more raw materials efficient than the Pidgeon process in China - based on reported operating data, RIMA sacrifices magnesium recovery to achieve a higher silicon efficiency by operating at stoichiometric silicon addition whereas the Chinese sacrifice silicon efficiency by overcharging silicon to achieve a higher magnesium recovery. However irrespective of these differences, raw materials utilization efficiencies are not materially different between these two thermal processes and are substantially less than stoichiometric efficiency for silicon reduction of dolime.

As such, the environmental benefits of the Bolzano process as shown in Table 6 are not due to materially higher process efficiencies compared to the Chinese fossil fuel based Pidgeon process but rather they are attributable to RIMA's specific situation including integrated production of FeSi and magnesium using hydroelectricity and charcoal produced from renewable eucalyptus trees grown in Brazil which provides a net GHG biofuel credit.

By comparison, the Zuliani Process shows significant improvements in raw material utilization efficiencies compared to all other Thermal processes. Hence, the environmental benefits reported in Table 6 for thermal conversion of dolomite to magnesium using the Zuliani Process with natural gas and hydroelectricity are fully transportable to any geographic region with high quality dolomite and similar clean energy sources.

## 6.2 Entry Gate to Exit Gate

D'Errico et al. [9, 14] report that conventional magnesium STEP 2 Entry Gate to Exit Gate product manufacturing generates an additional 19.4 kg CO<sub>2</sub> per kg, however this amount could be reduced to between 1 to 2 kg CO<sub>2</sub> per kg by replacing SF<sub>6</sub> with more environmentally friendly cover gas and by adopting near net shape casting technology such as semisolid thixocasting.

## 6.3 Exit Gate to Grave

The end of life savings in CO<sub>2</sub> from using lightweight materials in an average medium sized car can be determined based on the following assumptions [9, 14]:

Average car weight: 1300 kg

Average emissions: 2.85 kg CO<sub>2equiv</sub> per liter of gasoline consumed

Average fuel consumption: 8.5 liters per 100 km

For every 100 kg weight reduction, emissions are reduced by: 1.083 kg CO<sub>2equiv</sub> per 100 km

Average car lifetime: 200,000 km

Total CO<sub>2</sub> emissions over average car lifetime: 48,450 kg

From these assumptions the Exit Gate to Grave CO<sub>2</sub> savings from light-weighting can be determined as follows:

Exit Gate to Grave kg CO<sub>2</sub> Benefit = 1.083 \* (km travelled/100)\*(kg saved/100)

## 6.4 Overall Cradle to Grave Emissions

To achieve a net positive environmental benefit the emission savings from reduced vehicle weight must be counterbalanced by the added emissions required to produce the lightweight materials such as magnesium and aluminum. The following equation can be used to determine the net overall Cradle to Grave emissions reduction from light-weight materials substitution:

Total Savings kg CO<sub>2equiv</sub> = Exit Gate to Grave Benefit – (Cradle to Entry Gate + Entry Gate to Exit Gate)

## 6.5 Cradle to Grave Benefits from the Use of Magnesium Produced with the Zuliani-Gossan Process

Based on a detailed component by component analysis, USAMP [17] recently determined that a total of 159 kg of magnesium could be incorporated into the average North American car. This would represent an increase in magnesium usage by about 154 kg over the existing 5 kg usage; USAMP concluded that the estimate seemed reasonable given that the sum of all independent magnesium components developed by the date of the study was 173 kg.

USAMP estimated that there would be the following weight savings associated with the addition of 154 kg of new magnesium components:

- Straight substitution weight savings; a total direct substitution weight savings of about 132 kg can be realized by replacing 226 kg of cast iron and steel with 113 kg of magnesium (reducing weight by about 113 kg) and by replacing 59 kg of aluminum with 41 kg of magnesium (reducing weight by about 18 kg)
- Secondary weight savings; related to reductions in chassis, suspension and power train weights stemming from substitution weight savings. Secondary weight savings are less significant if part substitution is made on a “one of” basis. However, secondary weight savings are expected to be significant if major design changes are made as a result of significant light-weighting. In the USAMP study, a secondary weight saving of a further 95 kg is assumed to result from vehicle redesign efficiencies arising from the addition of 154 kg magnesium.

As such USAMP predicted a total weight savings of about 227 kg by replacing cast iron, steel and aluminum with 154 kg of magnesium.

Assuming modern and efficient STEP 2 SF<sub>6</sub> free, near net shape parts manufacturing can be adopted [9, 14], two Cases can be examined as follows;

Case 1: the 154 kg of magnesium parts are produced in China with the Pidgeon Process. In this case the Cradle to Exit Gate GWP for the magnesium parts will be 45.3 kg CO<sub>2</sub> per kg Mg or 6,976 kg CO<sub>2</sub> in total. Using the Exit Gate to Grave kg CO<sub>2</sub> Benefit equation in section 6.3 above with 227 kg weight savings, it can be determined that the vehicle must travel only just under 284,000 km before the “CO<sub>2</sub> generated” by the production of the parts from Chinese Pidgeon Process magnesium breaks-even with “CO<sub>2</sub> saved” from improved fuel efficiency resulting from the weight reduction.

Case 2: the 154 kg of magnesium parts are produced using magnesium produced by Gossan in Manitoba Canada with the Zuliani Process. In this case the Cradle to Exit Gate GWP for the magnesium parts will be 11.1 kg CO<sub>2</sub> per kg Mg or 1,709 kg CO<sub>2</sub> in total. Using the Exit Gate to Grave kg CO<sub>2</sub> Benefit equation in section 6.3 above with 227 kg weight savings, it can be determined that the vehicle must travel only just over 69,500 km before the “CO<sub>2</sub> generated” by the production of the parts from Gossan magnesium breaks-even with “CO<sub>2</sub> saved” from improved fuel efficiency resulting from the weight reduction.

Assuming the car’s estimated lifetime is only 200,000 km [9] in total, the net environmental benefit of using 154 kg of magnesium parts produced using magnesium from Gossan’s Zuliani Process would reduce the car’s lifetime CO<sub>2</sub> emissions by almost 7%.

## 7.0 Conclusion

Due to higher grade dolomite and improved process efficiencies, the Zuliani Process as would be practiced by Gossan Resources using hydro electricity and natural gas in Manitoba Canada, consumes only 9.67 kg dolomite and 0.85 kg of ferro-silicon per kg of Mg ingot produced, while Pidgeon Process in China uses 11.16 kg of dolomite and 1.19 kg of ferro-silicon per kg of Mg ingot produced. The overall recovery of magnesium from dolomite is 74.0 % for Pidgeon Process in China and 90.4% for the Gossan-Zuliani process.

Overall energy consumption for the Pidgeon Process in China and Gossan-Zuliani process are respectively 71,893 and 40,686 kcal/kg Mg ingot produced. The difference in energy requirements is due to use of less efficient coal in China compared to hydroelectric power for ferrosilicon production and magnesium reduction steps and natural gas for dolomite calcination step for Gossan-Zuliani process.

Based on detailed mass & energy balances developed in the study, the amount of carbon dioxide emission for the Pidgeon Process in China and Gossan-Zuliani process are determined as 42.0 and 9.1 kg CO<sub>2</sub>/kg of Mg ingot, respectively. The difference in the emission levels is due to higher raw materials utilization efficiencies, use of hydroelectric power for ferrosilicon production and magnesium reduction steps and natural gas for dolomite calcination step for Gossan-Zuliani process. There is no carbon dioxide emission for ferrosilicon production and magnesium reduction steps. Lower carbon dioxide emissions are produced during the dolomite calcination step as natural gas generates less carbon dioxide compared to coal for an equivalent heat requirement. The improvement from the Chinese Pidgeon Process’ GWP of 42.0 being reduced to the 9.1 GWP of the Gossan-Zuliani process is highly significant environmentally.

Assuming the use of clean energy and SF<sub>6</sub> free, near net shape parts manufacturing, magnesium produced with the Zuliani Process will significantly improve the environmental benefits associated with magnesium’s use in the automotive industry. Based on a Life Cycle Analysis, substitution of cast iron,



steel and aluminum with Zuliani process magnesium, at levels proposed (154kg) in the 2004 USAMP study, can reduce average midsize car emissions by almost 7% over the car's life expectancy. The LCA shows that the that such a vehicle needs to travel only just over 69,500 km before the "CO<sub>2</sub> generated" by the production of the parts from Gossan magnesium would break-even with "CO<sub>2</sub> saved" from improved fuel efficiency resulting from the weight reduction. This compares to a break-even distance of almost 284,000 km for the vehicle utilizing parts made from Chinese magnesium. Such performance is clearly advantageous compared to Chinese magnesium however most importantly it would place Gossan's magnesium ingot in a much more favorable environmental position vis-à-vis aluminum which has a somewhat higher GWP and provides on average between 20-30% less weight savings than magnesium.

## 8.0 References

1. H.S. Ray, R. Sridhar and K.P. Abraham, "Extraction of Nonferrous Metals". Affiliated East-West Press Private Limited, 1999.
2. E. Willet, "Magnesium", Rosen Publishing Group, 2007.
3. F. Cherubini, M. Raugei and S. Ulgiati, "Life Cycle Analysis of magnesium production: Technological overview and worldwide estimation of environmental burdens", Resources, Conservation and Recycling, Vol. 52, 2008, pp. 1093-1100.
4. C.H. Caceres, "Economical and Environmental Factors in Light Alloys Automotive Applications", Metallurgical and Materials Transactions A, Vol. 38A, July 2007, pp. 1649-1662.
5. N. Halmann, A. Frei and A. Steinfeld, "Magnesium Production by the Pidgeon Process Involving Dolomite Calcination and MgO Silicothermic Reduction: Thermodynamic and Environmental Analyses", Ind. Eng. Chem. Res., Vol. 47, 2008, pp 2146- 2154
6. Ditze and C. Scharf, "Recycling of Magnesium", Papierflieger Verl.: Clausthal-Zellerfeld, 2008.
7. S. Ramakrishnan and P. Koltun. "Global warming impact of the magnesium produced in China using the Pidgeon process, Resources, Conservation and Recycling, Vol. 42, 2004, pp. 49-64.
8. G. Feng, N. Zuo and W. Zhi-hong. "Assessing environmental impact of magnesium production using Pidgeon process in China", Trans. Nonferrous Met. Soc. China, Vol. 18, 2008, pp. 749-754.
9. F.D'Errico, G. Perricone and R. Oppio. "A New Integrated Lean Manufacturing Model for Magnesium Products", JOM, Vol. 61, No.4, 2009, pp. 14-18.
10. L.M. Pidgeon and W.A. Alexander, Trans AIME, vol. 159, 1944, pp.315.
11. Thanumarajah and P. Koltun, "Is There and Environmental Advantage of Using Magnesium Components for Light-Weighting Cars", Journal of Cleaner Production, Vol. 15, 2007, pp. 1007-1013.
12. S. Ramakrishna and P. Koltun "A Life Cycle Greenhouse Impact Study of Magnesium Ingot Production in Australia". Journal of Cleaner Production, 2004.
13. F.C.V. Franca and R.P Brito, "RIMA's Process: Green Magnesium from a Fully Integrated Plant", Proceedings of the 68<sup>th</sup> Annual World Magnesium Conference, Prague Czech Republic, May 8-10, 2011.
14. F.D'Errico, S. Fare and G. Garces, "The Next Generation of Magnesium Based Material to Sustain the Intergovernmental Panel on Climate Change", Magnesium Technology 2011, edited by W.H Sillekens, S. R. Agnew, N.R. Neelameggham and S.N. Mathaudhu, TMS (The Minerals, Metals and Materials Society) 2011, pp. 19-23.
15. T.E. Norgate, S. Jahanshahi and W.J. Rankin, "Assessing the Environmental Impact of Metal Processes", Journal of Cleaner Production, 2007.

16. International Aluminium Institute, 2000. Life cycle inventory of the world aluminium industry with regard to energy consumption and emission of greenhouse gases. [http://www.world-aluminium.org/iai/publications/documents/full\\_report.pdf](http://www.world-aluminium.org/iai/publications/documents/full_report.pdf), 2000.
17. USAMP Study “ Magnesium Vision 2020 – a North American Automotive Strategic Vision for Magnesium” December 7, 2004

## APPENDIX A- MASS BALANCES

### Mass Balance Calculation- Pidgeon process in China Process

Dolomite calcination:

		CaO	CaO	MgO	CO <sub>2</sub>	Others	Total
Before	Dolomite	Composition	27.80	19.98	43.63	8.60	100
		Mass (kg)	3.22	2.32	5.06	1.00	11.6
After	Dolime	% Composition	58.18	41.82			100
		wt (kg)	3.12	2.24			5.36

Ferrosilicon production:

		Si	Fe	Total
Ferrosilicon	% Composition	75.00	25.00	100.00
	wt (kg)	0.89	0.30	1.19

After Briquette:

	CaO	CaO	MgO	Total
Dolime	% Composition	58.18	41.82	100
	wt (kg)	2.96	2.13	5.09

		Si	Fe	Total
Ferrosilicon	% Composition	75.00	25.00	100.00
	wt (kg)	0.85	0.28	1.13

Magnesium reduction:

**Input:** Dolime and ferrosilicon

Output		CaO	MgO	SiO <sub>2</sub>	Others	Si	Fe	Mg	Total
Ferrosilicon	% Composition					44.49	55.51		100
	wt (kg)					0.23	0.28		0.51
Process	% Composition	64.0	6.75	29.25					100
	wt (kg)	3.12	0.33	1.42					4.87
Mg in Ingot	wt (kg)							1.00	
Recovery % of Magnesium in Ingot from Dolime								73.96	

#### Notes & Assumptions

The calculation basis is for 1 kg of magnesium

The composition of the Dolime was normalized

Dolime is the limiting reactant 1

Assuming only the ferrosilicon reduction reaction occurs

Assuming 8.75 % loss of Mg from crown to ingot

Assuming a 3.32% loss during the calcination process

Assuming a 5.0% loss during briquetting

APPENDIX A- MASS BALANCES (Continued)

Mass Balance Calculation- Gossan-Zuliani Process

Dolomite calcination:

			CaO	MgO	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub>	SiO <sub>2</sub>	LOI	CO <sub>2</sub>	Others	
Before	Dolomite	Composition	30.06	21.37	0.04	0.18	0.15	0.42	47.18	0.60	100
		Mass (kg)	2.95	1.96	0.00	0.02	0.01	0.04	4.61	0.06	9.67
After	Dolime	%	56.91	40.46	0.08	0.34	0.28	0.80	0.35	1.14	100
		wt (kg)	2.58	1.83	0.00	0.02	0.01	0.04	0.02	0.05	4.55

Ferrosilicon production:

		Si	Fe	Al	Others	Total
Ferrosilicon	% Composition	75.30	23.34	1.10	0.26	100
	wt (kg)	0.64	0.20	0.01	0.00	0.85

Magnesium reduction based on FactSage Model and Experimental Test Results:

Mg Recovery dolime to ingot: 90.4%

FeSi (75% Si) Utilization net of by-product FeSi for sale: 0.8390 kg per kg Mg ingot

## APPENDIX B- HEAT BALANCES

**Pidgeon process in China Process: Dolomite Calcination:**  $\text{CaCO}_3 \cdot \text{MgCO}_3 \leftrightarrow \text{CaO} \cdot \text{MgO} + 2 \text{CO}_2$

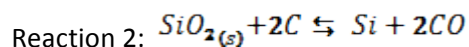
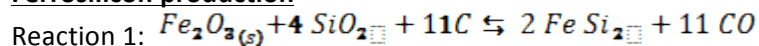
Compounds	$\Delta H^\circ$ (kcal/mole)	Moles/kg Mg	$\Delta H^\circ$ rxn (kcal/kg of Mg)
CaO*MgO*2CO <sub>2</sub>	-556	63	-34982
CaO*MgO	-297	63	-18705
CO <sub>2</sub>	-94	126	-11835
Heat of Reaction at 25 °C			
		4442	kcal/kg of Mg
Heat Required for products to reach 1200 °C			
Compounds	H <sub>1200</sub> -H <sub>298</sub> (kcal/mole)	Moles/kg Mg	$\Delta H$ (kcal/kg of Mg)
CaO*MgO	28	63	1775
CO <sub>2</sub>	14	126	1809
$\Delta H$			3584
Total heat Required			
		8026	kcal/kg of Mg

**Gossan-Zuliani Process- Dolomite Calcination:**  $\text{Ca CO}_3 \cdot \text{MgCO}_3 \leftrightarrow \text{CaO} \cdot \text{MgO} + 2 \text{CO}_2$

Compounds	$\Delta H^\circ$ (kcal/mole)	Moles/kg Mg	$\Delta H^\circ$ reaction (kcal/kg of Mg)
CaMg(CO <sub>3</sub> ) <sub>2</sub>	-556.00	52.43	-29149
CaO*MgO	-297.30	52.43	-15587
CO <sub>2</sub>	-94.05	104.85	-9862
Heat of Reaction at 25 °C			
		3701	kcal/kg of Mg
Heat Required for products to reach 1200 °C			
Compounds	H <sub>1200</sub> -H <sub>298</sub> (kcal/mole)	Moles/kg Mg	$\Delta H$ (kcal/kg of Mg)
CaO*MgO	28.21	52.43	1479
CO <sub>2</sub>	14.38	104.85	1508
$\Delta H$		2987	kcal/kg of Mg
Total heat Required			
		6688	kcal/kg of Mg

APPENDIX B- HEAT BALANCES (CONTINUED)

**Ferrosilicon production**



**Pidgeon Process in China- Ferrosilicon Production**

Reaction 1

Compounds	$\Delta H^\circ$ (kcal/mole)	Moles/kg Mg	$\Delta H^\circ$ rxn (kcal/kg of Mg)
Fe <sub>2</sub> O <sub>3</sub>	-197	3	-524
SiO <sub>2</sub>	-218	11	-2321
C	0	29	0
FeSi <sub>2</sub>	-19	5	-103
CO	-26	29	-775
Heat of Reaction 25 °C		1968	kcal/kg of Mg
Heat Required for products to reach 1723 °C			
Compounds	H <sub>1723</sub> -H <sub>298</sub> (kcal/mole)	Moles/kg Mg	$\Delta H$ (kcal/kg of Mg)
FeSi <sub>2</sub>	36	5	192
CO	14	29	397
$\Delta H$			589
Total Energy Required		2557	kcal/kg of Mg

Reaction 2

Compounds	$\Delta H^\circ$ (kcal/mole)	Moles/kg Mg	$\Delta H^\circ$ rxn (kcal/kg of Mg)
SiO <sub>2</sub>	-218	21	-4618
C	0	42	0
Si	0	21	0
CO	-26	42	-1121
Heat of Reaction 25 °C		3497	kcal/kg of Mg
Heat Required for products to reach 1723 °C			
Compounds	H <sub>1723</sub> -H <sub>298</sub> (kcal/mole)	Moles/kg Mg	$\Delta H$ (kcal/kg of Mg)
Si	9	21	183
CO	14	42	574
$\Delta H$			757
Total Energy Required for reaction 2		4254	kcal/kg of Mg



Total Energy Required for process	6811	kcal/kg of Mg
-----------------------------------	------	---------------

**Gossan-Zuliani Process- Ferrosilicon Production**

Reaction 1:

Compounds	$\Delta H^\circ$ (kcal/mole)	Moles/kg Mg	$\Delta H^\circ$ reaction (kcal/kg of Mg)
Fe <sub>2</sub> O <sub>3</sub>	-196.70	1.90	-375
SiO <sub>2</sub>	-217.70	7.62	-1658
C	0.00	20.95	0
FeSi <sub>2</sub>	-19.40	3.81	-74
CO	-26.42	20.95	-553
Heat of Reaction 25 °C			
		1405	kcal/kg of Mg
Heat Required for products to reach 1723 °C			
Compounds	H <sub>1723</sub> -H <sub>298</sub> (kcal/mole)	Moles/kg Mg	$\Delta H$ (kcal/kg of Mg)
FeSi <sub>2</sub>	36.07	3.81	137
CO	13.53	20.95	283
$\Delta H$		420.73	kcal/kg of Mg
Total Energy Required			
		1826	kcal/kg of Mg

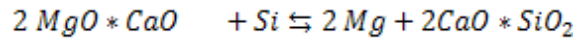
Reaction 2

Compounds	$\Delta H^\circ$ (kcal/mole)	Moles/kg Mg	$\Delta H^\circ$ reaction (kcal/kg of Mg)
SiO <sub>2</sub>	-217.70	15.15	-3298
C	0.00	30.30	0
Si	0.00	15.15	0
CO	-26.42	30.30	-801
Heat of Reaction 25 °C			
		2498	kcal/kg of Mg
Heat Required for products to reach 1723 °C			
Compounds	H <sub>1723</sub> -H <sub>298</sub> (kcal/mole)	Moles/kg Mg	$\Delta H$ (kcal/kg of Mg)
Si	8.63	15.15	131
CO	13.53	30.30	410
$\Delta H$			541
Total Energy Required		3039	kcal/kg of Mg
Total Energy Required for process		4865	kcal/kg of Mg

APPENDIX B- HEAT BALANCES (CONTINUED)

Pidgeon Process in China

Magnesium Reduction



Compounds	$\Delta H^\circ$ rxn (kcal/kg of Mg)	
Input Raw Materials	-13924	
Outputs	-13035	
Heat of Reaction 25 °C	996	kcal/kg of Mg
Heat Required for products to reach 1200 °C		
$\Delta H$		3180
Total Energy Required	4561	kcal/kg of Mg

Gossan-Zuliani Process

Compounds	$\Delta H^\circ$ rxn (kcal/kg of Mg)	
Input Raw Materials	-13529	
Outputs	-12595	
Total Heat Generated	935	kcal/kg of Mg
Heat Required for products to reach 1600 °C		
$\Delta H$	3687	kcal/kg of Mg
Total Energy Required	4622	kcal/kg of Mg

## APPENDIX C- CO<sub>2</sub> EMISSION CALCULATIONS

Dolomite calcination:

	Pidgeon Process in China	Gossan-Zuliani Process
Source of Energy	Coal	Natural Gas
Heat Input (kcal/kg Mg ingot)	12541.0	10517.5
Heat Loss (kcal/kg Mg ingot)	4514.8	3829.4
Amount of Coal (67.5%)or Natural Gas (kg/kg of Mg)	2.0	0.8
Amount of CO <sub>2</sub> released (kg/kg of Mg)	5.0	2.3
Amount of CO <sub>2</sub> released from reaction (kg/kg of Mg)	5.5	4.2
Total CO <sub>2</sub> from Process (kg/kg of Mg)	10.5	6.6

Ferrosilicon production:

	Pidgeon Process in China	Gossan-Zuliani Process
Source of Energy	Coal based electricity	Hydroelectric
Heat Input (kcal/kg Mg ingot)	16352.0	11680.0
Heat Loss (kcal/kg Mg ingot)	9541.4	4864.7
Amount of Coal (kg/kg of Mg)	0.9	0.6
Amount of CO <sub>2</sub> released (kg/kg of Mg)	14.7	2.2

Magnesium reduction:

	Pidgeon Process	Gossan-Zuliani Process
Source of Energy	Coal	Hydroelectric
Heat Input (kcal/kg Mg ingot)	43000.0	18488.1
Heat Loss (kcal/kg Mg ingot)	37940.0	13866.1
Amount of Coal (63% C) Or Natural Gas used (kg/kg of Mg)	6.8	0.0
Amount of CO <sub>2</sub> released (kg/kg of Mg)	15.9	0.0

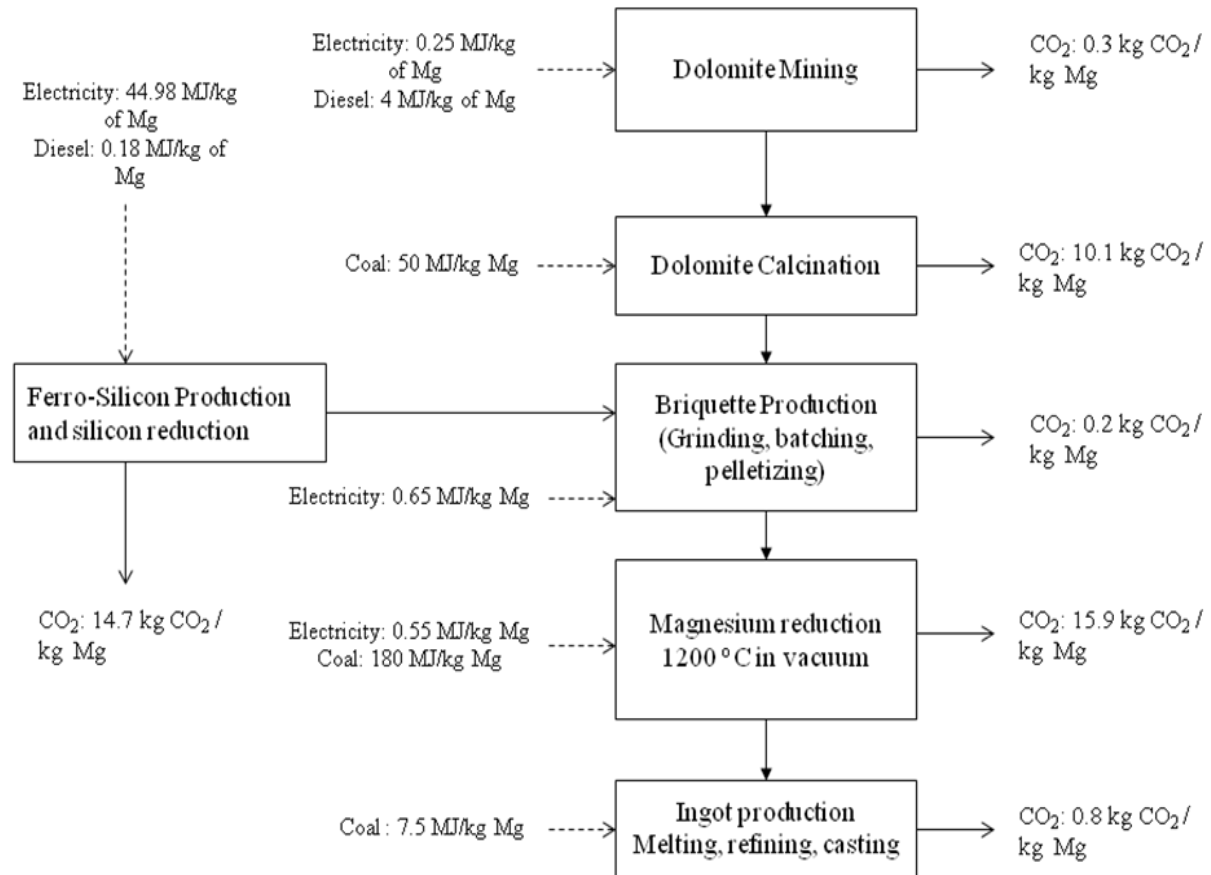
Magnesium Ingot Production

	Pidgeon Process in China	Gossan-Zuliani Process
Source of Energy	Coal- electricity	Hydroelectric
Heat Input (kcal/kg Mg ingot)	1793	1120
Heat Loss (kcal/kg Mg ingot)	1506	840
Amount of Coal (63% C) Or Natural Gas used (kg/kg of Mg)	0.3	0
Amount of CO <sub>2</sub> released (kg/kg of Mg) *	0.63	0

\* Additional CO<sub>2</sub> will be produced during ingot production in the Pidgeon Process in China due to melting of solid crown resulting in a CO<sub>2</sub> level of ~0.7 kg/kg of Mg

## APPENDIX D- PROCESS FLOW DIAGRAM

### Pidgeon Process in China



APPENDIX D- PROCESS FLOW DIAGRAM (CONTINUED)

Zuliani Process

