Status and potentials of magnesium production in China: Life cycle analysis focussing on CO_{2eq} emissions

Simone I. Ehrenberger Stephan A. Schmid Shaobo Song Horst E. Friedrich

German Aerospace Center (DLR)

Worldwide, production technologies for magnesium differ depending on geographical situation. China produces about three quarter of primary magnesium, but the Pidgeon process as used there in the past was shown to have high CO_{2ea} emissions per kg pure Magnesium. Now, production processes in China have changed significantly in the last years, and the phase out of $SF₆$ is well on its way worldwide.

We analyse the present situation based on recent data for the use of producer gas/coke gas and improvements in process parameters in China and give an outlook on further improvements for the Mg production technology chains. Changing the energy carriers for heating from coal to gas can reduce the greenhouse gas emissions up to 45 %. We conclude on the break-even distance from the comparison of an A-pillar strut mounting made from Mg with a steel component.

1 Introduction

Magnesium (Mg) production and use has had an unsteady history: the yearly worldwide outputs as well as production technologies have changed many times [1]. Due to differences in feedstock, also production technologies differ worldwide, depending on the geographical situation.

During the 1990s, Chinese Mg manufacturers began to renew the thermal reduction process also known as Pidgeon process. Due to large mineral resources, cheap manpower and low investment costs, Chinese companies have been able to produce at lower prices than other market participants using electrochemical processes. As a result, China is the market leader for primary Mg today. Figure 1 shows the market shares of Mg producing countries worldwide from 1995 to 2006. During this period, China's share rose from 25 % to almost 75 %. In 2007, its production volume amounted to 627,300 t [2].

The Pidgeon process requires considerable amounts of energy for heating purposes. For reasons of economic and ecological efficiency, efforts have been made during the last years to decrease the consumption of primary energy carriers. But technological chances in the Chinese Mg industry are also driven by political guidelines. The current five-year plan provides a reduction of energy consumption of 20 % per unit gross domestic product (GDP). This moved the China Nonferrous Metals Industry Association (CNIA) to decide on specific energy reduction measures in this industry branch. For Mg production, it announced a maximum consumption of 7 t standard coal per t Mg [3].

Figure 1: Primary magnesium world production

In our study we aim to assess the emissions of greenhouse gases (GHG) resulting from the Pidgeon process. Thus we modelled this
technology using data from Chinese technology using manufacturers and compared the use of coal for

heating with the utilisation of gaseous fuels. Finally, we extend our study to the comparison of Mg as car component material with steel and aluminium.

2 Status of Production Technologies

2.1 Electrolysis

Electrochemical processes to make Magnesium are based on salts containing chloride which can be found naturally or are transformed from other raw materials like serpentine, magnesite, bischofite or carnallite. The magnesium chloride salts are dried with various processes in order to receive anhydrous MgCl₂, either in solid or molten form.

For economic reasons, several electrochemical plants have been closed down in the past. Today, there are three plants in operation in Western countries: US Magnesium (US), Dead Sea Magnesium (Israel), and Rima in Brazil. Four plants are producing in the former Soviet Union (CIS). Dismantling of Norsk Hydro Becancour magnesium plant in Quebec, Canada has started. The Magnola plant (Quebec) originally set up to recover magnesium from asbestos tailings but not operated since 2003, is also scheduled to be taken down. In contrast to this, construction of a new plant in Russia to process tailings from Uralasbest has been started in late 2007 [4].

1. Preparation of raw material

2.2 Silicothermic Reduction

The silicothermic reduction of Mg using ferrosilicon (FeSi) as reduction agent is the only Mg production process used in China at present. It is named Pidgeon process after his inventor, the Canadian chemist Lloyd M. Pidgeon.

Figure 3 shows an overview of the process steps. Due to its abundant deposits, the raw material for Mg production in China is magnesium-calcium carbonate dolomite $(MgCO₃ \text{CaCO}₃)$. Thus, the first production step is the mining and transportation of dolomite to the Mg production site. In order to eliminate carbon dioxide $(CO₂)$ from the crystal structure, the rock material is treated in continuous rotating or batch furnaces at temperatures of about 1,000 °C, which is called calcination step. The calcined material is then grounded into fine powder and mixed with reaction agents. FeSi, which is consumed in considerable amounts, is added as reduction agent, while calcium fluoride $(CaF₂)$ works as catalyst. Calcined dolomite and agents are pressed into briquette form and put into the reduction furnace. At temperatures around 1,300 °C and under vacuum, the following chemical reaction occurs:

$$
2 MgO \cdot CaO + Si(Fe) \rightarrow 2 Mg + Ca_2SiO_4 + Fe
$$

Figure 2: Different routes of the electrochemical process

The raw Mg sublimates in the water cooled part of the furnace and is removed at the end of this batch process. As these so called Mg crowns still contain certain amounts of impurities, the last step of the Pidgeon process is the refining, where the Mg crowns are melted and treated with purifying agents.

Protection agents are needed to prevent the melted Mg from burning as it is highly combustible. Formerly, sulphur hexafluoride, the most potent greenhouse gas known, has been commonly used for such purposes. Recently, its use is phasing out, as there are alternative protection agents available with lower global warming potential. Chinese Mg companies use sulphur or fluxes containing small amounts of sulphur for preventing the Mg melt from burning.

Figure 3: Overview of Pidgeon process

Though the Pidgeon process has received remarkable improvements concerning energy consumption and emissions during the last years, there is still a considerable potential for enhancing its efficiency. Subjects of study are, for instance, the performance of furnaces, the handling of retorts, the use of waste heat or the further use of production waste. Energy consumption, as addressed in our study, is of special interest and there is an obvious movement from using coal to running the process with gaseous fuels.

An overall process improvement can be achieved by integrated production of several commodities. This means, that there is no need for material transports and the possibility of using by-products from one process as input for others. Concerning the Pidgeon process, it would be favourable to install local production networks combining the production of primary energy with a FeSi and a Mg plant. Coke production, for instance, which is needed for the making of FeSi, comes along with the production of a considerable amount of coke oven gas which can be used for heating furnaces in a Mg plant.

3 Data Survey in China

There are few publications on greenhouse gas emissions for Chinese primary Mg, e.g. [5], [6], [7], [8]. As the production of Mg during the last decades has been dominated by electrochemical processing and thus first life cycle analyisis (LCA) studies on its environmental impact refer to this technology which is not representative for present Mg supply, these papers are the first to indicate the dimension of GHG or $CO₂$ emissions from Pidgeon process. Considering the changes mainly in energy consumption but process efficiency as well, we aim to reflect this with a new model for the Mg production process and evaluate the potential for overall $CO₂$ reduction.

In order to obtain an idea of how the technological improvements link to the reduction of $CO₂$ emissions of the entire production chain, we surveyed the 14 companies with highest primary Mg production capacity in China, most of them located in the provinces Shanxi and Ningxia. By sending them a standardized questionnaire, we ensured a consistent set of data on energy consumption and material inputs of each production step of the Pidgeon process. The questions addressed in detail qualitative as well as quantitative information on energy carriers used for each process step. Material requirements have been asked as well, specifically concerning reduction and refining agents. Additionally, we asked for possible future technology improvements concerning the use of other energy carriers than coal and the implementation of new reduction process systems. We further interviewed company employees who were in charge of the said questionnaire by telephone or via e-mail. Most of our contact persons are technicians, two work at administration offices and one is employed at the trade department. Of the 14 producers six provided us with data. These companies represent a production capacity of 178,000 t Mg per year which would be 31 % of the real annual Chinese Mg output in 2007. Some of the companies are planning or constructing new Mg facilities, so that a further increase in Mg production output can be expected. For three companies we could not find contact information.

Additional three do not produce primary Mg themselves, one company had no contact person with adequate knowledge available and another did not send the questionnaire back in time. Furthermore, we sent a similar questionnaire to two FeSi producers which provide the Mg companies with this material. Both returned us data on the energy and material demand for their product.

4 LCA models of Chinese Magnesium Production

4.1 Concept of technology evolution for energy consumption

For the cradle-to-gate assessment of Mg production in China we assume an output of 1 kg Mg ingot for each process option. We calculated the material and energy flows for the Mg production steps as well as the supply of operating and raw materials using the software tool Umberto [9]. The main process regarding the way of Mg from mining to ingot casting consists of five steps as described above. Except from the mining of dolomite, we modelled these processes according to the data we got from Chinese producers. Company data are also used for the FeSi production process. For the calculation of energy and material requirements for other processes we referred to public databases. Most of the processes calculated in our life cycle model represent present Chinese conditions. Some minor material supply processes refer to global or European average data, which have only marginal effect on the overall results. In order to show the progress of development in production technologies, we identified three technology stages:

- Solid fuel use
- Energy switch: gaseous fuel
- Integrated plants

As the thermal reduction is an energy intensive process, 51 - 57 % of the emitted GHG stem from the utilization of fossil energy carriers for fuelling issues or as electricity in plants using merely coal ([5], own calculations). Therefore, reduction of energy consumption and alternation of fuels are the most promising strategies for avoiding GHG emissions. Due to the target set by the CNIA, the utilization of gas produced from coal is seen as new technology standard and the companies we surveyed plan to implement such process improvements if not already done. The fuel gas can either be coke oven gas or producer gas. Some of the companies still use coal in addition to gas, mainly because of operational issues in the calcination step. To show some effects of implementing gaseous fuels, we compared its use to coal and evaluated the benefits for three different types: producer gas, coke oven gas and natural gas. Additionally, we assessed the effect of integrating coke and FeSi production into a Mg plant.

Solid fuel use: coal

This group represents manufacturers using coal directly as energy source for heating the furnaces. Apart from company information, we used also data from literature [5] for modelling this process version and obtained four different datasets. The coal input for fuelling for the overall process from calcination to refining varies between 8.2 and 9.5 kg per kg Mg.

Use of Producer Gas

Producer gas is the product of air and sometimes steam injection into coal. Main components are carbon monoxide (CO), hydrogen (H_2) and methane (CH_4) . The amount of producer gas needed for the entire Mg production process varies from 6 to 19 m³ depending on the amount of coal used additionally. This scenario is represented by three manufacturers.

Use of Coke Oven Gas

Coke oven gas is a by-product form coke production which is obtained from pyrolysis of coal. Thus, the emissions from coke oven gas production should only take into consideration the gas itself and not to the overall coke processing. Therefore we allocated the amount of emissions to air according to the energy content of all products from coke production (coke, coke oven gas and tar) what leads to a 15 % of energy input and emissions for the gas. In our model, the Mg production requires about 5.1 m³ coke oven gas per kg Mg plus a certain amount of coal for conventional furnace heating. One company is represented in this scenario.

Integrated plant

For some plants, a reduction of the overall energy consumption is achieved by implementing waste heat utilisation. This plant version also represents a local production network combining the production of coke and coke oven gas with a FeSi and a Mg plant. From the experiences of one company, a reduction of energy consumption for fuelling of 4.5 % can be assumed. Such an integrated production is not widespread yet, but nevertheless we obtained data from one manufacturer.

Use of Natural Gas

In addition to the "real" life energy supply for Mg production, we assumed the utilization of natural gas as substitute for coke oven or producer gas. It is not used in present Chinese plants as it is significantly more expensive than the other gases mentioned. Due to its higher energy content, the amount of natural gas needed would be lower compared to other fuel gases. As this is a theoretical consideration, we calculated the amount of natural gas needed according to the information on the use of other fuel gases in an advanced Pidgeon process assuming the energy need to be equal. This reference process corresponds with the integrated process described above in terms of energy efficiency due to waste heat utilisation. Thus, the natural gas scenario does not represent present Mg production but a further and presumably bestcase $CO₂$ reduction potential by using an alternative energy carrier.

4.2 Inputs for process steps

As the conversion rates from dolomite to calcined dolomite and from raw Mg to pure Mg hardly vary, we assumed them to be equal for each scenario. Material transport is calculated from Mg producer information and differs considerably between production sites. The data input for the main life cycle steps are explained in detail in the following.

Dolomite mining: This process is taken from the ecoinvent database [10] which is commonly used in LCA. These data present a large uncertainty, but due to the lack of alternative information they have been used in this study. The transportation of the raw material to the Mg production plant is calculated according to the average distance between dolomite mine and plant for each scenario.

Calcination: For the calcination process we used the input of 2 kg raw per kg calcined dolomite. The energy need is supplied by either coal or coke oven gas or producer gas or a combination of different energy carriers, depending on the scenario. For calcination there is still a certain amount of coal required for some production alternatives due to the specific energy feed in this process.

Briquetting: The briquetting system represents the mixing of the calcined dolomite with the additives FeSi and CaF₂. The demand of FeSi is similar for all data sources and amounts to 1.1 to 1.3 kg per kg Mg. Concerning the production of FeSi, we calculated an average production option according to the data provided by surveyed manufacturers and literature [11]. The use of $CaF₂$ varies from 0.01 to 0.26 kg per kg Mg and thus differs for the scenarios. Besides these additives, this process requires a certain amount of electricity ranging from 0.18 to 0.33 kWh per kg Mg.

Reduction: The reduction process is compared to all other production steps in an Mg plant the most energy intensive. It requires a considerable amount of coal, coke oven gas or producer gas for heating the reduction furnaces. Additionally, the material needs for retorts are calculated as the retort have a life time limited to a maximum of 90 days. For this study we assumed an average output for one retort of 25 kg and a life time of 60 days.

Refining: During refining the melted raw Mg is cleaned from impurities before casting the pure Mg ingot. Apart from energy for melting the Mg, flux agents are needed for refining and protection purposes. The amount of added flux agents varies from 0.08 to 0.13 kg per kg Mg.

4.3 Results for Greenhouse Gas Emissions

For the evaluation of the Pidgeon process' environmental performance, we calculated the greenhouse gas emissions resulting from fossil resources. Figure 4 shows the results for all scenarios. As the FeSi production is associated with a considerable amount of $CO₂$ emissions due to its high energy consumption, the result for this material is shown separately. As for FeSi production as well as for dolomite mining, all Mg production options are based on equal input data, there is only one bar for these life cycle steps displayed. The black lines at the FeSi bar indicate the changes in emissions considering different transportation distances. A minimum of nearly 0 km is achieved in integrated plants.

Clearly, the production of FeSi, the calcination of dolomite and the reduction itself are the most emission intensive life cycle steps. The results for the coal scenario correspond with the results found in [5] and [6], where coal is the only energy input for heating as well. The overall emissions amount to 47 kg CO_{2eq} for the conventional coal using option. The uncertainty lines for the coal and producer gas scenario indicate the minimum and maximum values obtained from our calculations and represent different Mg plants and material transport distances. The emissions decrease gradually with the utilisation of producer and coke oven gas and with the implementation of an integrated

plant. The lowest GHG emissions we calculated stem from the natural gas scenario and amounts to about 25 kg CO_{2ea} . Considering the decrease of emissions in the different process steps, the reduction process bears much more reduction potential than calcination. To a certain extent this is because of the $CO₂$ emissions from chemical reaction during calcination, which amount to 5 - 6 kg per kg Mg and which cannot be avoided. Another reason is that there have been made more efforts in increasing the efficiency of the reduction process as this directly influences recovery rate and quality of the raw Mg. This has clearly succeeded and similar efforts could lead to a further reduction of emissions from other process stages as well.

Considering the studies about Mg production by electrolysis mentioned in chapter 2.1 and taking into account the phase out of SF_6 utilisation, the GHG emission from this technology still improves our findings about the advanced Pidgeon process.

Figure 4: Greenhouse gas emissions from Pidgeon process

5 Evaluation of Magnesium application in cars – A-pillar Concept

For the assessment of the application of Mg for vehicle construction, we extended our Pidgeon process model in order to consider a car component made from Mg. Figure 5 shows images of an Mg A-pillar strut mounting.

Figure 5: Examples of highly integrated Apillar strut mountings from Mg (DLR)

For the production of this component, the Mg has to be alloyed first. For the considered automotive application, the AM50 alloy is the most appropriate. We modelled its production similar to the production of the Mg ingots, but adding Al with a share of 5 % and Mn of $<$ 1 % (for our study, we assumed a Mn share of 0.9 %). The weight of the A-pillar is 6 kg. For modelling the production process, we took data from three Chinese companies we interviewed and which produce Mg alloy and assumed the further processing of the alloy ingots being performed in Germany. These further production steps consist mainly of material transports and of die casting which we modelled using data from the ecoinvent database. The entire production chain for the A-pillar Mg amounts to 174 kg $CO₂$.

For the use phase we considered an average middle class car, represented by the VW Golf, and the use of gasoline as fuel. To evaluate the potential for reducing $CO₂$ emissions by using this car component, we compared it with a

reference part which has exactly the same function concerning its technical performance in the vehicle's construction. This reference is an A-pillar made from steel which weights 12.6 kg. The production data represent an European average and are taken from the ecoinvent database and the life cycle inventory database of the International Iron and Steel Institute. From this we calculated the $CO₂$ emissions from the production of the steel component (80 kg $CO₂$).

Apart from different production technologies for the Mg and steel components which come along with different energy and material consumptions. the weight of the car components plays a major part for the comparison of their life cycle. Approximately 0.38 l per 100 km can be saved per 100 kg weight reduction in an average middle class car [12].

For the comparison of the A-pillar from Mg and steel we first modelled its production as described above and then evaluated the fuel savings by weight reduction. As the Mg component weights 6.6 kg less than the steel one, this means a reduction of fuel consumption of 0.025 l per 100 km. We calculated the overall $CO₂$ emissions over the entire production chain from resource extraction to car use to assess the gross emissions for both components for a certain amount of driven km.

Figure 6 shows the $CO₂$ emissions for the use phase for both A-pillars up to a driving distance of 200,000 km which is a reasonable mark for a gasoline car's lifetime. Starting point of the lines

is the $CO₂$ emissions resulting from the production itself. In chapter 4 we have discussed the GHG emissions for different Ma production options. These are represented as a best-case Mg scenario (use of natural gas). But unlike in chapter 4 we do not take into account other GHG emissions than $CO₂$.

The grey line represents the reference component. The vertical line marks the breakeven point with the best-case Mg scenario using natural gas (green line). The point of intersection is at about 136,000 km. For the average mere coal using Pidgeon process (red line), the breakeven point is beyond 200,000 km. These results show that changes in Mg production and thus its $CO₂$ emissions have great impact on the breakeven distance, although the emissions from the use of gasoline during driving are presumed to exceed those of component manufacturing by far. In addition to decreasing the emissions from Mg production itself, there is a certain reduction potential in the component manufacturing as well. Regarding the energy requirements for melting the raw material, it would be more efficient to melt the Mg only once. For that the pure Mg and Mg alloy making as well as the diecasting process would have to take place at one single production site.

Another aspect would be the effect of end-of-life options which we do not address in this study. Regarding the fact, that Mg recycling would save more than 90 % of the energy used for its primary production [13], this would also have

Figure 6: Break-even distance for A-pillar from steel and Mg

great impact on the $CO₂$ performance of the car component. The production of such components requires high quality alloy, therefore different grades of magnesium scrap become important. Nevertheless, considering further uses of Mg after its application in a vehicle would change the $CO₂$ emission balance and possibly improve the break-even distance for such components when compared to steel.

6 Conclusions

The examination of the present Pidgeon process in China has lead to the following basic findings:

- Compared to literature data of electrolysis using water power as energy source, the silicothermal reduction provides GHG emission rates which are up to eight-times higher (6 kg GHG per kg Mg [14] versus 47 kg in our coal scenario).
- Technological improvements alone, especially for the reduction process, can lead to significant reduction in GHG emissions as recent data from Chinese companies show.
- Changing in addition the energy carriers from coal to gas can reduce the GHG emissions by $\overline{45}$ % to 25 kg CO_{2eq}/kg Mg assuming a best-case scenario using natural gas in an energy efficient plant.

In our study we deal with selected points of the Pidgeon process only. It would be favourable to obtain a more comprehensive view of the Chinese average Pidgeon process.

Our calculations regarding the exemplary use of Mg as a highly integrated A-pillar strut mounting show a break-even distance of 136,000 km for the comparison with steel. Considering end-oflife options for Mg could potentially lower this distance.

The results demonstrate that magnesium can have life cycle advantages over steel, provided that its processing is developed carefully. Evidence from Chinese producers shows that important steps have been taken which need to be applied throughout the sector.

7 Literature

1. Friedrich, H.E. and B.L. Mordike, eds (2006): *Magnesium Technology. Metallurgy, Design Data, Applications*. Springer.

- 2. International Magnesium Association (5/2008): *Update Weekly, Newsletter*.
- 3. China Magnesium Association (2008): *Online Information, http://www.chinamagnesium.org/detail.php?id*
- *=3445*. [cited 2008 02/22]. 4. USGS (2007): *MAGNESIUM IN THE THIRD QUARTER 2007*, in *Mineral Industry Surveys*, D.A. Kramer and K.K. Hermanson.
- 5. Ramakrishnan, S. and P. Koltun (2004): *Global warming impact of the magnesium produced in China using the Pidgeon process.* Resources, Conservation and Recycling. 42(1): p. 49-64.
- 6. Zang, J.C. (2001): *The Pidgeon Process in China and its Future*, in *Magnesium Technology*, Mineral, Metals and Materials Society: New Orleans, USA.
- 7. Gao, F., Z. Nie, Z. Wang, and T. Zuo (2006): *Resource depletion and environmental impact analysis of magnesium produced using pidgeon process in China.* Chinese Journal of Nonferrous Metals. 16(8).
- 8. Gao, F., Z. Nie, Z. Wang, and T. Zuo (2007): *Environmental Assessment of Magnesium Production using the Pidgeon Process in China*. in *8th International Conference of Eco-Materials*, Brunel University.
- 9. ifu *Umberto. Software for Process Optimisation, Material Flows and Environmental Management, and Life Cycle Assessment.*, Institute for Environmental Informatics Hamburg GmbH: Hamburg.
- 10. ecoinvent (2006): *Project ecoinvent data v2.0. The Life Cycle Inventory Data Version CD ROM*, Swiss Centre for Life Cycle Inventories.
- 11. Zulehner, W., B. Neuer, and G. Rau (2005): *Silicon*, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley.
- 12. Espig, M., M. Johannaber, and R. Wohlecker (2006): *Simulation der Verbrauchsverbesserung durch Gewichtsreduzierung in Pkw.* ATZ. 108(12).
- 13. Hanko, G., H. Antrekowitsch, and P. Ebner *Recycling Automotive Magnesium Scrap.* Journal of Materials Processing Technology. February 2002.
- 14. Albright, D.L. and J.O. Haagensen (1997): *Life cycle inventory of magnesium*. in *IMA 54: Magnesium Trends*, Toronto, Canada: International Magnesium Association.