Mintek Thermal Magnesium Process (MTMP): Theoretical and Operational Aspects

M. Abdellatif
Mintek, Randburg, South Africa

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Abstract – Extensive testwork on atmospheric thermal magnesium production has highlighted certain important fundamental and operational factors that have a major influence on magnesium extraction and its extraction rate, the condensation efficiency of magnesium, as well as on the quality of the condensed metal. The possible impact of these factors on the selection and preparation of raw materials, recipe choice, furnace electrical energy consumption, and on the refining requirements of the crude magnesium is discussed. Selected pilot plant operational and metallurgical data are also presented.

INTRODUCTION

Magnesium production in China has been expanding for the last ten years or so, reaching a stage where China effectively controls the supply of magnesium. Chinese dominance may be attributed to several factors, four of which are—

1. The low cost of raw materials, particularly ferrosilicon
2. A cheap and abundant labour force
3. Inexpensive coal and energy
4. Safety, health, and environmental standards that are lower than those in Europe and the US

These factors make it possible for the Pidgeon process[1] to succeed in China, in spite of its being a batch and labour-intensive process. However, it is doubtful that similar success can be attained and sustained in the Western world because of unfavourable market conditions. The high energy prices and labour costs effectively forced the recent closure of plants at both Pechiney and North West Alloys, the two major thermal magnesium producers. Other considerations included environmental factors and low magnesium prices. In addition, the relatively low magnesium price forced several projects that aimed at using the electrolytic process to be abandoned. High capital costs and environmental concerns also have contributed in this regard.

The Mintek thermal magnesium process (MTMP) could offer an economically viable alternative to the Chinese Pidgeon process. The MTMP process has been

described previously by Barcza *et al.*[2-4] and Schoukens[5]. This paper gives some fundamental details of the process.

FEATURES OF THE PROCESS

The MTMP is based on DC open-arc smelting of calcined dolomite (dolime) at atmospheric pressure in the presence of ferrosilicon (Figure 1). As such, the process is not constraint by the electrical resistivity of the slag and allows operating the furnace at relatively high voltage (Table I gives some furnace operational data from the pilot plant at Mintek). The volatilized magnesium is captured as liquid metal in a surface condenser, which permits periodic tapping of the crude magnesium. Doing so, in conjunction with conditions at atmospheric pressure, makes possible the operation of a large-scale facility 'continuously' (or semi-continuously).
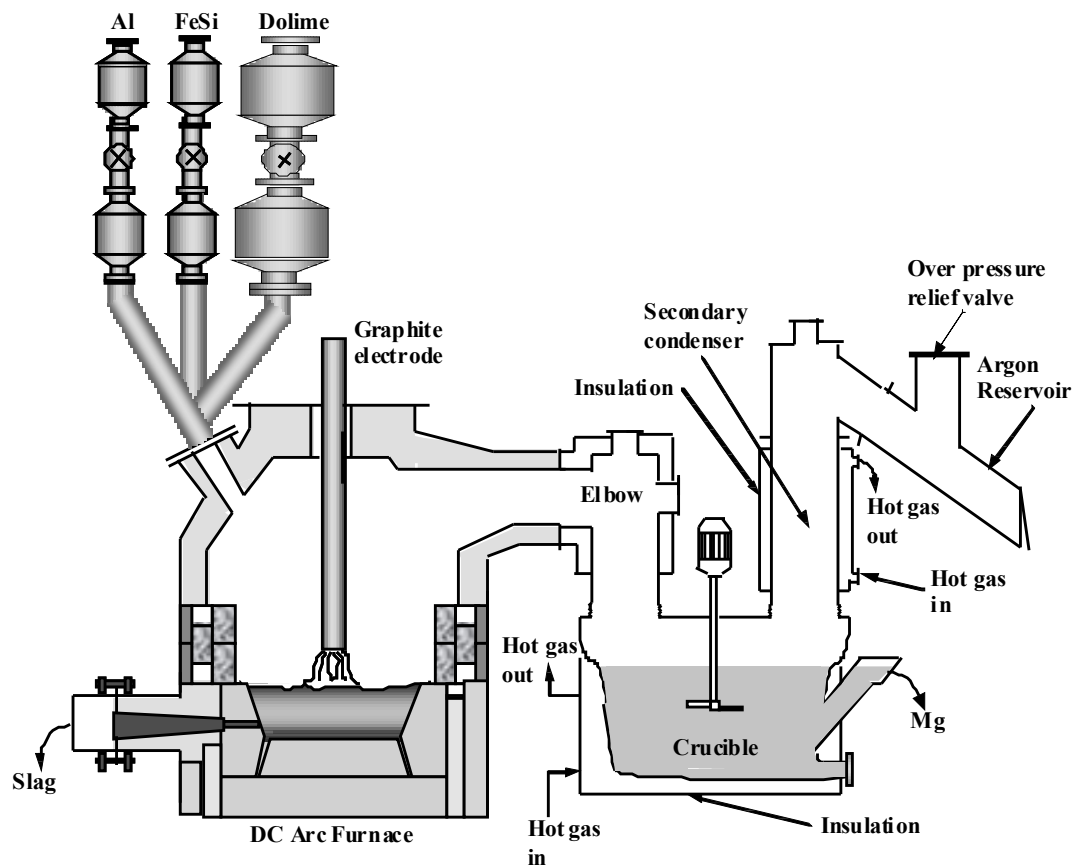

Figure 1: General layout of the MTMP process

Operating at atmospheric pressure offers other advantages over the Pechiney (0.05–0.1 atm) and Pidgeon (0.1 mmHg) processes:

1. Impurity levels in the crude magnesium could be lower. Impurities include Al, Ca, but most importantly Si, Fe, Ni, Cu, and Mn, which are difficult and expensive to remove.

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2. The driving force for the condensation of magnesium vapour is raised considerably, as the vapour pressure in the incoming bulk-gas phase is nearly atmospheric.

3. The potential risk of air-ingress into the system is largely eliminated in a process carried out at atmospheric pressure. Continuous slag tapping—*i.e.* through an overflow-weir arrangement—eliminates the need for oxygen lancing and can prevent the ingress of air during the tapping operation. Thus, oxidation of volatilized magnesium is minimized, and so fewer oxides and nitrides of magnesium form in the condenser.

4. Carbothermic reduction of magnesium might be insignificant as the graphite electrode is not in direct contact with the slag. Compare this with resistance heating by the submerged-arc practice at Pechiney. This is significant in several ways, including—
   - Possibly lower electrode consumption
   - Thus less frequent electrode addition, which increases the overall plant availability
   - Better magnesium recoveries in the condenser where the reversion reaction is minimized

$$CO + Mg_{(v)} = MgO + C \qquad [1]$$

   - Notice that coalescence of the condensed magnesium droplets is adversely affected by the presence of carbon

5. Condensation to a liquid phase reduces the energy requirements in the cleaning and refining stages, as re-melting of the crude magnesium is not be required.

Table I: Furnace Operating Conditions

Condition	July 2003 Campaign
Total feed rate, kg/h	525
Dolime	440
Ferrosilicon	56
Aluminium	29
Dolime feed temp, °C	650
Batch mass, kg	1310
Operating power, kW	760
Operating voltage, V	160
Power density[1], MW/m²	0.75
Current density[2], A/cm²	19
Arc length, mm	100 to 250
Maximum slag depth[3], mm	430 to 460
Argon flow rate, l/min	40 to 50
Furnace pressure, mmH₂O	–5 to –15

1: Based on an original furnace inside diameter of 1200 mm
2: Based on a graphite electrode diameter of 200 mm
3: At the end of feeding a batch of raw materials

Certain issues however may require consideration:

1. Operating the process at atmospheric pressure decreases significantly the average gas velocities in the system. This is beneficial in limiting feed carry-over, and thus dross (oxide) formation in the condenser. However, there is a concern that low gas velocities might lower the magnesium mass-transfer rate onto the condensing surface.
2. Condensing to a liquid phase implies that the condensing surface needs to be maintained at relatively high temperatures (>650ºC), which could require a larger condensing area, as energy- and mass-transfer rates (from the bulk gas onto the condenser surface) could be lowered.
3. In order to achieve an economically acceptable level of magnesium extraction and rate of Mg(v) generation, the furnace operating temperature needs to be increased above that employed in Magnetherm and Pechiney processes. Electrical energy consumption could, therefore, be higher.
4. As the furnace is operated in the open-arc mode, side-reactions in the arc-attachment zone might be severe. Of concern is the volatilization of iron, aluminium (if used), manganese, silicon, and nickel. These elements tend to dissolve in the condensed magnesium; they hard to remove in the refining stage. In addition, the formation of volatile sub-oxides of aluminium and silicon could result in the oxidation of magnesium vapour, either in the furnace freeboard or in the condenser, according to

$$SiO(g) + Mg_{(v)} = MgO + Si \qquad\qquad [2]$$
$$Al_2O(g) + Mg_{(v)} = MgO + 2Al \qquad\qquad [3]$$

These reactions add to dross formation, increase the levels of silicon and aluminium in the crude magnesium, and thus to refining costs.

MAGNESIUM EXTRACTION

DC-arc smelting of magnesium-containing raw materials at atmospheric pressure is influenced by several factors, including temperature, choice of feed recipe, slag depth relative to furnace diameter, and the reactions in the arc-attachment zone (AAZ). As indicated previously, the furnace operating temperature needs to be above 1600°C; it could be as high as 1800°C in order to—

1. Achieve an economically acceptable degree of magnesium extraction and rate of extraction
2. Allow continuous slag tapping, yet keep the consumption of furnace electrical energy as low as possible

As the slag bath is not agitated externally, uniformity of the slag temperature could become an issue: segregation of high-melting slag components and their possible freezing on the furnace side-walls and/or on the hearth could take place. Were this to happen, continuous slag tapping might be interrupted. One

way to overcome such a potential difficulty is by optimizing the ratio of slag depth to furnace internal diameter. In addition, the operating voltage can also be varied in order to take advantage of the stirring effect of the arc, which thus maintains a more uniform bath temperature. In practice, this means that the arc length can change dramatically should a frozen hearth be suspected or the thickness of the freeze lining become excessive.

Changing the arc length could have an impact on the chemical reactions taking place in the AAZ, particularly on those reactions that lead to the generation of undesirable species such as $Al_2O_{(v)}$, $SiO_{(v)}$, and $Mn_{(v)}$. Whereas long arcs (relatively high voltage and low current) suppress the tendency of such species to form, short arcs (low voltage and high current) may have the opposite effect. The effect of side reactions is even worse when the furnace is kept idling at power levels close to energy-loss levels, without feeding, for extended period of time. Such practices result in severe volatilization of $Al_2O_{(v)}$, $SiO_{(v)}$, and other species. If furnace off-gas is directed into the condenser during such idling periods, impurity levels in the crude magnesium increase.

The slag temperature should also take into account the furnace free-board temperature and, more importantly, that of the furnace off-gas. The gas leaving the furnace needs to be above the boiling point of magnesium (1107°C) in order to prevent its premature condensation in the ducting leading to the condenser. Higher off-gas temperatures also suppress reactions between refractory (normally alumina-based) on the roof of the furnace and magnesium vapour:

$$Al_2O_3 + 3\ Mg_{(v)} = 2\ Al + 3\ MgO \qquad [4]$$

Thermodynamically, reaction 4 takes place at temperatures below about 1480°C. It contributes to magnesium losses and to increased levels of aluminium in the condensed metal.

Clearly, the operating temperature is controlled largely by the feed recipe employed, but more specifically by the resulting slag composition. The feed recipe could consist of dolime and/or magnesia as the source of magnesium, and ferrosilicon and/or aluminium as the reducing agent(s). In addition, and depending on the prevailing market conditions, fluxing agents could be employed as a means of lowering slag-tapping temperatures, and possibly of increasing magnesium extraction. Table II gives typical chemical compositions of the raw materials used in MTMP pilot-plant tests, and Table III lists selected physical properties of the dolime.

Dolime-based recipes—where the main slag constituent is di-calcium silicate—can be processed at temperatures from 1550–1750°C. [6, 7] The slag could contain 2–15% Al_2O_3, depending on aluminium additions (Table IV shows typical results obtained at pilot scale). On the other hand, magnesia-based recipes produce di-magnesium silicate slag, and may thus demand an operating temperature of 1700–1800°C. [6, 8] The addition of dead-burnt lime (5–10% CaO in the slag), calcined bauxite (5–15% Al_2O_3 in the slag), or aluminium (as part of

the reductant) is beneficial in keeping the slag tapping temperatures below 1800°C.[6]

Table II: Typical chemical analyses of raw materials, mass per cent

Dolime			Ferrosilicon	Aluminium
Component	Mass %	Component	Mass %	Mass %
MgO	37.49	Mg	NA	NA
Al_2O_3	1.34	Al	0.74	99.80
CaO	55.60	Si	76.70	0.06
SiO_2	3.33	Ca	0.05	NA
Fe_2O_3	1.55	Mn	0.13	0.016
MnO	0.03	Ni	0.015	0.001
NiO	0.015	C	0.03	NA
C	0.05	—	—	—
H_2O	<0.10	—	—	—

Table III: Selected physical properties of dolime

BET surface area, cm²/g	10–700
Relative density	3.0–3.2
Particle size, mm	6–25

Particle size of FeSi and Al is 6–12mm

Table IV: Typical furnace results

Slag analyses, mass per cent:	July 2003 Campaign
MgO	4.9–8.5
Al_2O_3	12.1–14.8
SiO_2	17.0–20.6
CaO	54.0–57.0
Slag temperature, °C	1650
Mg-extraction, %	82
Extraction rate, kg/h/m²	85
Electrode consumption, kg/MWh	1.5
Thermal efficiency, %	66

In addition to decreasing the consumption of electrical energy, lower operating temperatures reduce the severity of the arc-side reactions (in the AAZ). These reactions are also affected by factors such as the power flux, the arc length (voltage-current), and the activity of certain slag components (i.e., SiO_2, Al_2O_3, MnO). One way to minimize the formation of gaseous sub-oxides and

undesirable metal vapours is decrease the ferrosilicon addition (Figure 2). This depends on whether a lower degree of magnesium extraction can be tolerated.

The ratio of bath depth to furnace diameter could become important when continuous slag tapping is practised. The furnace should provide sufficient reaction time — on average 3 to 4 hours, depending on the choice of feed recipe and the operating temperature — in order to achieve the target extraction at a relatively high extraction rate.
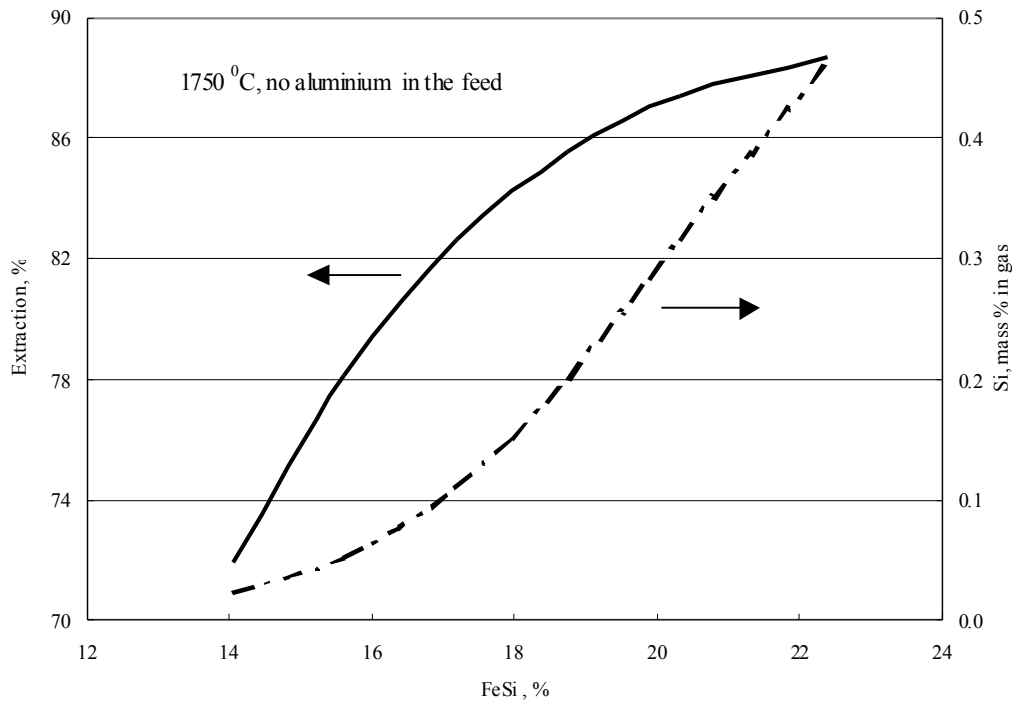

Figure 2: Influence of FeSi addition on magnesium extraction and silicon content in the furnace off-gas. Pyrosim calculations[9]

CONDENSATION

The condenser design and its operation need to meet the following conditions:

1. The condenser should capture the volatilized magnesium as liquid. This requirement is important: it allows continuous, or semi-continuous, tapping of the produced metal in a commercial facility. Doing so improves the overall plant availability and thus the economics of the process. In order to capture the magnesium as liquid, the condensing surface and the holding compartment of the condenser are required to operate at temperatures above the melting point of the magnesium. Indeed, the presence of solids (dusting in the furnace, MgO, Mg_3N_2, etc) will increase the required operating temperature to 700–750°C. In addition to contributing to system blockages and pressure build-up, condensation to a solid tends to be of a dendritic form, which exhibits a large surface area, a

property that makes it amenable to oxidation upon contact with air (air leakage, oxygen lancing, CO from the furnace, *etc.*).

2. The condenser should tolerate small amounts of solids that can be removed from the condenser upon tapping the liquid magnesium. Depending on such factors as the rate of air ingress, dusting, and carbothermic reduction of MgO in the furnace, the solids could constitute up to 5% of the crude metal mass (typically, 1–3%).

The rate and efficiency of condensation depend on several factors. Principal among them are (1) the surface area of the condenser and its temperature, (2) the partial vapour pressure of magnesium in the bulk gas and at the condensing surface, and (3) the average gas temperature and its velocity. The surface area for condensation needs to be large enough to condense all the magnesium vapour to liquid for prompt tapping. The area should also be capable of dissipating the energy of condensation to the cooling medium. For operational and costs reasons, however, the area should be as small as possible. Although the pilot-plant condenser was designed for 50 kg $Mg_{(v)}$/h/m², a full-scale condenser should be able to handle 70–120 kg $Mg_{(v)}$/h/m², provided that the above-mentioned factors are properly addressed.

As mentioned earlier, the operating temperature of the condenser could be from 700–750°C. Temperature has an impact on the transfer rates of mass and energy, which could imply that the required specific surface area may need to be larger than those used at Pechiney.

The partial pressure of magnesium vapour at the condenser inlet is nearly atmospheric (if we assume that the flow rate of argon is kept to a minimum of 20–100 l/min, and that the total system pressure is atmospheric). At the condensing surface, however, its partial pressure could be very low (2.6–15 mm Hg, depending on temperature). Therefore, the average velocity of the gas needs to be high enough to ensure that bulk diffusion of magnesium vapour into the surface is fast. Note that condensation could result in a local vacuum that leads to the rapid flow of gas, which may cause relatively large mass- and energy-transfer rates compared with those estimated from semi-empirical correlations.

Because the condensation process takes place gradually, the average gas velocity, its temperature, and the partial pressure of magnesium in the bulk gas all change as the gas flows through the condenser assembly. For example, at the condenser inlet the temperature might be as high as 1400°C with a magnesium partial pressure of more than 0.99 atm (when the total pressure is 1 atm). At the outlet, the gas temperature and magnesium partial pressure could drop respectively to 650–700°C and 2.6–6.6 mm Hg. (Table V presents selected operational data and metallurgical results obtained from testwork on the pilot plant. Table VI shows a typical crude-magnesium analysis.)

Table V: Operational and Metallurgical Results of the Pilot Plant Condenser

Inlet gas, kg/h	60–85
Inlet gas velocity, m/s	1.3–1.8
Inlet P_{Mg}[1], atm	0.81–0.83
Condenser wall temp. at gas inlet, °C	700–1100
Condenser wall temp. at gas outlet, °C	300–400
Condenser crucible temp. °C	
Inside	500–900
Wall	400–650
Outlet gas velocity, m/s	0.035–0.05
Outlet P_{Mg}, atm	0.02–0.05
Magnesium condensation rate, kg/h	65–70
Condenser efficiency, %	75–80

1: Local atmospheric pressure = 0.85atm

Table VI: Chemical Analyses of the Crude Magnesium, ppm

Element	Al	Ca	Si	Fe	Mn	Ni
As tapped	260	1750	550	80	190	50
Salt-treated	125–300	100–250	200–510	130–450	140–200	40
AST Grade B-92	500	500	500	500	1000	10

RAW MATERIALS

In general, selection of the feed material should be based upon the requirements of the furnace and condenser. These include—

1. Minimum energy. This can be achieved by, for example, charging the dolime and/or magnesia as hot as possible.
2. Optimum magnesium extraction and extraction rate. Factors that affect magnesium extraction include furnace operating temperature, pressure, average retention time (ratio of slag depth to diameter, total feed rate, continuous vs batch tapping, etc.), chemical composition of feed materials, and the choice of feed recipe used.
3. Minimum dusting (feed carry-over and arc-side reactions). Strong particles coarser than 2 mm (preferably 6–30 mm) would minimize dusting.
4. Liquid-phase condensation to facilitate periodic, or continuous, removal of the crude magnesium. The operating temperature of the condenser should be slightly higher than the melting point of magnesium. However, because of the presence of some solids, the temperature of the condenser may need to be as high as 750°C.
5. Inert gas. Argon is introduced into the feed system of the furnace, the electrode seal, and other ports to prevent the condensation of magnesium

on such cold surfaces. The flow rate of inert gas needs to be kept to a minimum so that it does not affect to an appreciable degree the rate and efficiency of magnesium condensation. Note that high partial pressures of the inert gas tend to increase the magnesium extraction in the furnace.

The magnesium-containing feed component can be calcined dolomite (Tables III and IV) or calcined magnesite (magnesia). These can be processed in a rotary kiln to accomplish the following:

1. Removal of the carbon dioxide and moisture.
2. Volatilization of certain impurities, including halides, alkali metals, sulphur, tin, zinc, and lead.
3. Production of strong and dense particles with minimum specific surface area.
4. Controlled particle size.

The calcining of dolomite usually requires a kiln operating at 1380–1420°C, whereas the production of magnesia could require a calcining temperature of 1600°C, or higher. The kiln can be heated up by burning coal, coke, or natural gas, depending on the availability and costs. It is believed that both dolomite and magnesite require a retention time of 30–50 minutes in the hot zone of the kiln in order to meet the requirements listed above.

Asbestos tailings can also be employed as the source of magnesium. However, safety and environmental considerations make its use in magnesium production a challenging option.

Dolime (and magnesia, when used) should contain as little metal oxides such as Fe, Cr, Mn, Ni, Ti, and Cu as possible. These oxides are readily reduced by the reducing agent(s) employed, and thus increase the consumption of both electrical energy and reductant. Relatively high levels of silica are also undesirable as it may affect the MgO activity in the slag. This could be the case when, for example, dolime is used where the molar ratio of CaO to MgO in the starting feed recipe is less than unity, and where the addition of dead burnt lime is not possible for economic or operational reasons. Preferably the lime should be free of carbon and moisture, have a low specific surface area, comprise large and strong particles, and should be fed hot into the furnace—at 700°C and higher.

Manganese and nickel contents in the raw materials should also be controlled to a minimum, as they are volatile at the smelting temperatures used. As such they report to the condensed magnesium, which makes the condensate difficult and expensive to refine. Pilot-plant testwork carried out to date suggested that between 3 and 5% of these two elements report to the crude magnesium.

Zinc, sodium, and potassium are even more volatile and, to a large extent, will end up in the condenser and report to the crude metal. They tend also to

condense on cold surfaces downstream of the condenser, where they could present a potential risk by exploding if they are not fully combusted.

Carbon, manganese, and nickel in the reducing agent(s) are undesirable for the reasons stated. Lumpy ferrosilicon containing 75– 80% Si is usually used as the reductant, but an alloy containing 90% Si could offer advantages such as increased silicon utilization and lower energy consumption. However, cost consideration may prevent the use of a high-Si alloy. The particle size and size distribution of the reductant(s) should aim at achieving the desired extraction and extraction rate; it should do so with the minimum amount of dusting from disintegration, whether it take place within the feed system, or in the furnace (Tables III and IV).

Although current market conditions dictate that the use of aluminium should be eliminated, aluminium has desirable effects. It produces in a more flowable slag and increases the activity of MgO in the slag. This is important when continuous slag tapping is practised. Reduced energy consumption, faster kinetics, and possibly higher extraction are among the other benefits of the addition of aluminium (Figures 3 and 4).
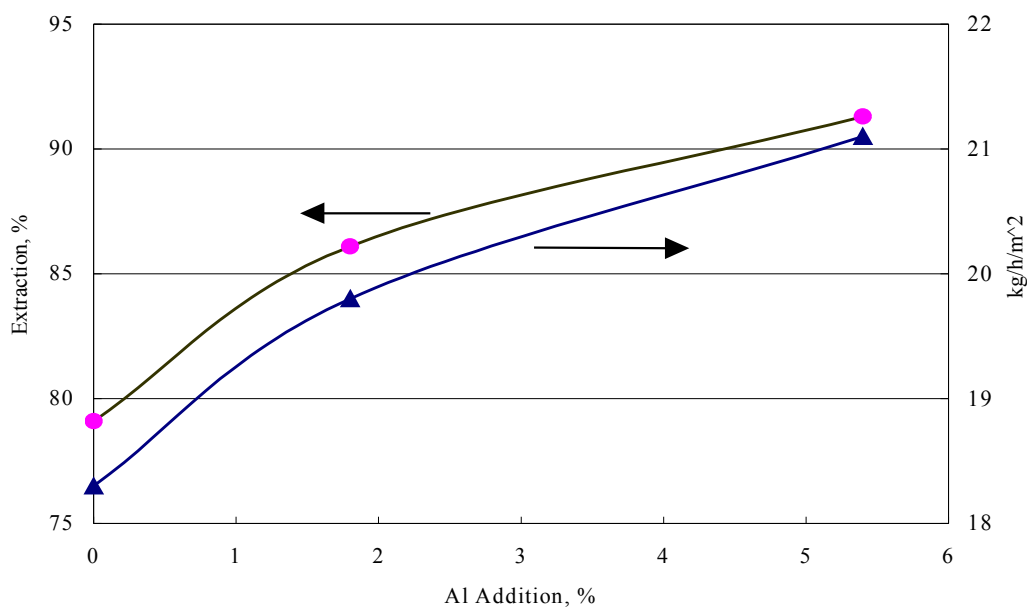

Figure 3: Magnesium extraction and extraction rate vs aluminium addition. 40-kW furnace, 1700°C, 5 kg/h, FeSi addition adjusted to give 89% extraction as predicted by Pyrosim[9]
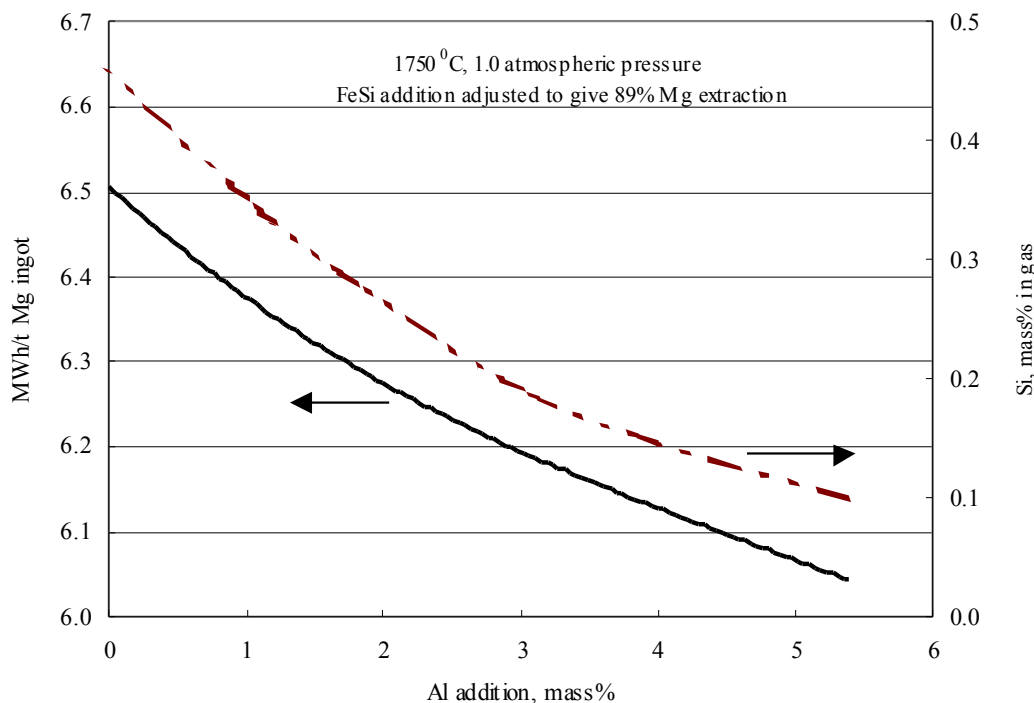
Figure 4: Influence of aluminium addition on energy consumption and silicon content in the furnace off-gas. Pyrosim calculations[9]

CONCLUSIONS

Magnesium extraction and extraction rate are dependent, in part, on the operating temperature and the feed recipe used; they need to be optimized in order to improve the economics of the process. For this purpose, the furnace needs to be operated in such manner as to produce and deliver almost pure magnesium vapour to the condenser.

Capturing the volatilized magnesium in a liquid state is crucial to the continuous operation of an industrial facility. For prompt tapping and for low cleaning and refining costs the condensed metal should contain as little solids as possible. The proper selection and preparation of raw materials could contribute to achieving high condensation efficiency, to improving the quality of crude magnesium, and hence to minimizing refining costs.

ACKNOWLEDGEMENTS

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