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# Evolution of the Magnetherm Magnesium Reduction Process

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## Abstract

The magnetherm process was developed and implemented as an improvement of the solid state silicothermic magnesium reduction process. This process was used commercially for over 35 years. The reduction plant operation and equipment are described as they existed at the time of the industry wide curtailment.

## Introduction

The chemical reaction for all silicothermic methods [1] for producing magnesium from dolomite is the same:

$$2CaOMgO + Fe\,Si\,75\% \rightarrow Ca2SiO4 + 2Mg \uparrow\ + FeSix$$

The major differences are in the method of heating the mass to the reaction temperature, >1200 deg. C., the pressure in the reactor, and the condenser design. Under these conditions of temperature and pressure, magnesium is release in a gaseous form and condensed in either a liquid or solid phase.

The Magnetherm process was commercially operated from 1964 until 2005. Over the years of operation significant improvements were made to the process. The following is a brief description of that evolution.

## Equipment Description

Raw Material Feed System
Northwest Alloys Inc. Shut-down of commercial operation was the fall of 2001.[2] At that time, the entire furnace assembly required a footprint of approx. 90' H x 50' W x 75'D. The furnace and feed tanks extended over 47 feet in height. The other plus 40 feet were required for the movement of the radio controlled cranes and the loaded feed containers that filled the furnace feed containers. Typically there were three raw material feed tanks.

Each feed tank rested on a load cell system in order to monitor the dynamic change in the mass of the tank as the process runs through its cycle of operation. Below each tank was an isolation valve and a feeder. The ferrosilicon tank had a screw feeder. All other feed tanks used vibrating feeders. Pipes extend from each feeder discharge to a common collection vessel which had a single pipe leading to the furnace.

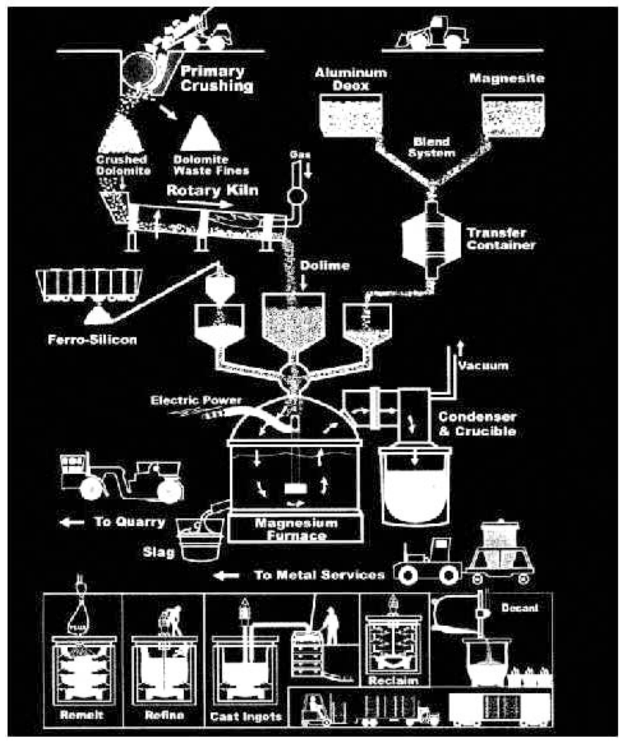


Figure 1. Schematic of Magnetherm Operations

Furnace
The furnace, a large cylindrical stainless steel vessel was lined with insulating refractory followed by carbon blocks for the inner lining. Carbon paste was rammed between the refractory bricks and carbon blocks tying the refractory components together. The top of the furnace was a refractory lined hemisphere. A water cooled copper electrode entered at the top of the furnace and was suspended above the carbon hearth. The side of the furnace nearest the raw material system had a flanged opening that allowed the feed system to be attached to the furnace. Directly opposite this opening was an exhaust port or tuyere from which the magnesium vapor exited to the condenser assembly.

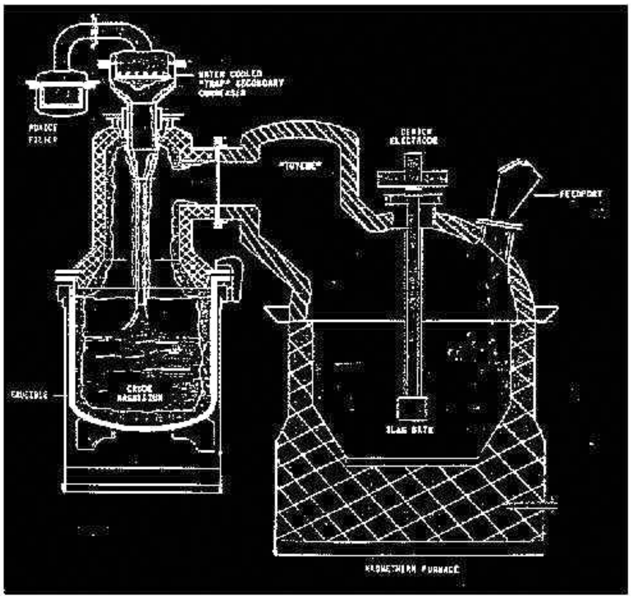


Figure 2. Cross Section of Magnetherm Furnace and Condenser

The furnace was heated by passing an electrical current through the molten slag. A single phase AC transformer provided electrical power to the furnace. The top electrode was connected to one output of the power transformer. Six water cooled electrodes (sole electrodes) were radially located in the prebaked carbon blocks constituting the floor of the furnace. They were connected to the other output of the power transformer. Great care was taken in establishing the length and position of the buss connecting the electrodes to achieve the correct impedance ensuring proper electrical balance. Power input was controlled by changing the winding output (tap) of the transformer. The transformer was a 15 MVA, rated at 90,000 amperes and 165 volts AC. A multiple of 3 operating furnaces were needed to maintain the phase balance on the utility company power supply transformer.

To remove slag from the furnace, two tap ports were located at the base of the furnace shell. A silicon carbide sleeve penetrated from the taping port flange into the body of the furnace providing an exit path for the molten slag and residual ferrosilicon.

The entire exterior of the furnace was water cooled by a combination of sprays, over flow weirs and water cooled flanges to maintain a freeze zone of slag within the furnace. Water cooling was critical in maintaining the freeze zone of slag and to protect the outer shell from penetration by molten ferrosilicon. Periodic sandblasting of the operating furnace shell was required to remove scale buildup and ensure proper heat transfer.

Condenser

Magnesium vapor produced during furnace operation was condensed in a water cooled crucible (3 inch thick wall). A transition unit, called the elbow, joined the crucible to the furnace. It consisted of a double walled steel cylinder bolted to the top of the crucible. Mating flanges joined the elbow to the furnace. A support assembly on the side of the cylinder permitted the unit to be suspended on a wheeled cart that allowed the entire condenser assembly to be moved into or away from the furnace. A water tank, hung on the flange of the elbow-crucible assembly, provided the water cooling for the steel crucible.

A steel pipe extending from the top of the elbow to a point just below the crucible flange allowed for non-condensable vapors to flow through the elbow assembly to the vacuum system (see figure 2). The funnel shaped top of this unit (trap) extended above the top of the elbow to function as a secondary magnesium condenser. The cone was topped with a domed lid (trap lid) that had an internal baffle to deflect residual magnesium vapor to the cool surfaces of this vessel. Vapors leaving the trap passed through the pumice filter, which protected the vacuum system from magnesium metal and pyrophoric metals such as sodium and potassium condensing in the vacuum lines. A large diameter flexible braided stainless steel pipe extended from the side of the filter canister attaching the condenser assembly to the vacuum system.

Vacuum System

. The entire furnace system from the raw material container lid to the exhaust on the vacuum pump was operated to maintain 70 torr measured at the furnace. Two particulate filters (90 micron and 10 micron) were located in series prior to the vacuum pump. Each furnace had a dedicated positive displacement vacuum pump that maintained pressure throughout the operating cycle. For the most part rubber “o” rings made the seal between mating flanges. If the system was exposed to heat, the flanges were water cooled.

Argon was fed to the raw material tank to maintain a pressure gradient from the top of the feed system to the feed port, to the vacuum system. This gas also assisted in directing the magnesium to the condenser on start up.

Center Electrode

A single electrode provided power to the furnace. This consisted of a flange for sealing to the furnace, a copper pipe and a graphite head attached to the base by cast bronze. To prevent melting the copper, an inner pipe carried cooling water down the center discharging cool water to the electrode head, flowing up the sides of the copper shaft, and out at a side discharge at the top of the electrode. Refractory blocks placed around the exterior of the electrode provided added protection.

**Operation**

The process was a batch operation consisting of a two part cycle. The first half consisted of feeding out the mass of dolime with a stoichiometric amount of other feed materials in the fixed containers. The process interruption termed minor consisted of: bringing the furnace and dolime fixed container back to atmospheric pressure, refilling the dolime container, taping slag and drawing the system back down to operating pressure for restart. The 2nd half operation consisted of feeding out the recharged dolime and its associated feed materials and stopping operations to allow the furnace assembly to be reconditioned. This major downtime included bringing the furnace pressure to atmospheric, the tapping of the slag, removal of the full condenser and elbow assembly, and refurbishing the furnace with additional feed materials, clean parts, and a fully pressure checked system ready for a new operation cycle.

At the beginning of the furnace cycle, the furnace was at its minimum slag level. A new condenser was in place, vacuum prefilter tubes were cleaned, the raw material tanks were full and all ports were cleaned, closed, tightened.

The procedure for verifying that a furnace was ready for operation consisted of: holding the furnace at caloric power input and opening the valve to the vacuum system. The furnace assembly was evacuated to the target pressure for leak evaluation. The entire system was then isolated and held for a period of time. The pressure inside the system was observed and if it remained within a target level, the furnace system was deemed to be free of air leaks and it was ok to proceed with the cycle. If a leak was indicated, the system was once again, drawn down to target pressure and held. At this time the isolation valve located between the raw material feed system and the furnace was closed. The pressure in each zone was then observed and the one exhibiting a leak was identified. The system was then pressurized to slightly above atmospheric and the operators physically inspected the area for the source of the leak. Once found the problem was resolved and the furnace was again pressure tested. After passing the pressure test, the system was subjected to another drawdown evaluation.

Once the system was confirmed as leak free, the power was increased to the furnace, argon was fed to the dolime tank and the feeders activated to move raw material from the storage tanks into the furnace. The power and the rate that material was fed to the furnace were steadily increased until a target level was reached or the condenser performance showed that its maximum potential had been reached. Raw material input continued at this steady state until all the dolime was emptied from the dolime tank and the furnace was full of slag. During this steady state portion of the cycle, furnace and condenser conditions were monitored for changes in pressure and/or temperature, indicating problems. The feed system was monitored to ensure the material draw down rate was consistent. Deviations from the expected rate of weight loss could indicate blockages in the feed system. These incidents would necessitate opening the feed system to clear the blockage.

With the first half of the feed cycle completed, the power fed to the furnace was decreased to calorific level or shut off. The furnace was brought up to atmospheric pressure by isolating the system from the vacuum system and switching to a low pressure-high flow argon source. Once the furnace reached atmospheric pressure, the door at the base of the furnace and the feed port at the top of the furnace were opened. The clay plug sealing the furnace was drilled followed by use of an oxygen lance to burn a path into the molten furnace slag. Once slag flow was established, the slag level in the furnace was monitored through the feed port. Once the desired level was reached, a clay plug was forced into the tap hole stopping slag flow and a final slag level was measured. The flanges on the open ports were clean and sealed, readying the furnace for continuing operation. The dolime feed tank was refilled with hot dolime from the kiln while the slag tap was in progress.

Once the furnace was closed and all work completed, the furnace was once again tested for pressure integrity. If all was well, the second half of furnace operations began. Exposure of the condenser to air, while tapping slag and refilling the dolime tank after the first half of the cycle resulted in the degradation of condenser efficiency. This reduced the rate at which the furnace could be fed during the 2nd half of the cycle. As the condenser filed the raw material feed rate had to be decreased to accommodate the reduced efficiency.

If all went well, the dolime tank would be empty and the furnace would be full of slag for the second time in the cycle. Power was turned off or reduced to low level, the vacuum system was isolated from the furnace and argon was used to raise the furnace pressure. Many refurbishing operations occurred simultaneously: the feed port was opened; the tapping door opened; the raw material tanks opened and the condenser backed away from the furnace. The condenser assembly was removed to be serviced. The condenser crucible full of magnesium was covered and transported to the ingot casting department (Metal Services) for further processing. The raw material tanks were refilled. The slag was tapped. The feed port and the tuyere openings were cleaned of buildup. Once all ports were cleaned and opened to the desired size, the slag level in the furnace lowered to the desired level and the raw material tanks full, a cleaned condenser assembly placed on the furnace and all ports closed, the cycle was ready to be repeated.

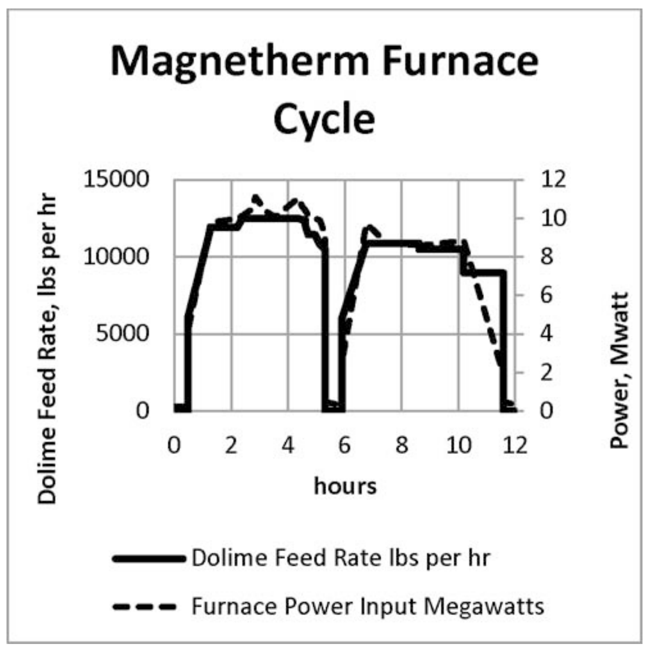


Figure 3. A typical magnetherm cycle of power and dolime feed to the furnace over time.

## Process Evolution

Early Days

Work began in France in 1948 to improve the silicothermic reduction process to produce magnesium.[3,4,5] The aim was to utilize the raw materials directly without having to produce a briquette and to be able to operate with less manpower and better thermal efficiency. This led to the development of a resistance furnace where current passing through the slag provided the source of heat. By adding alumina to the raw material mix a lower melting point slag was obtained.

The first successful furnace began operation in 1955 and produced 200 kg of magnesium per day. The unit connecting the furnace to the collection crucible was the condenser which was preheated to 675 deg. C by means of a internal electric heating element. This allowed liquid magnesium to be collected in the crucible which was cooled with water sprays. Evacuation took place off the back of the crucible.

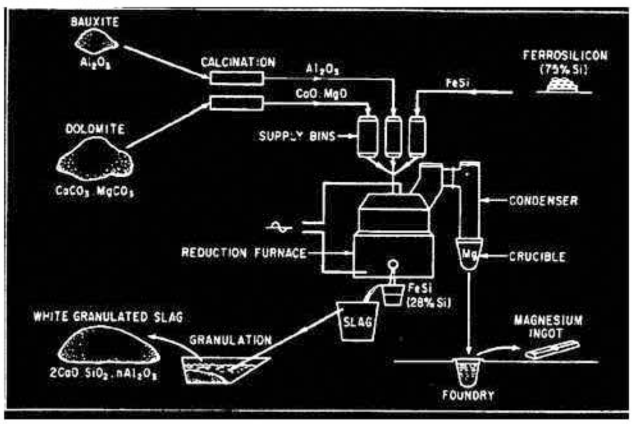


Figure 4. Original process schematic

An attempt was made to change from a single phase furnace power source to a three phase power source in 1956. This was unsuccessful in that it was difficult to balance the phases.

From 1957 through 1964 three separate furnaces were constructed. Each time the power supply was increased in size resulting in higher productivity. During this time frame the ability to use hot dolime directly from the kiln was incorporated into the design.

Prior to 1962 feed rates were volumetrically controlled. In 1962 material feed rates were monitored by overall tank weight changes. for improved raw material control. At the same time bauxite was substituted for the alumina.

Throughout the development period, furnace lining was undergoing frequent change. Owing to the aggressive nature of the slag and the reaction of magnesium with carbon, it was determined that a frozen layer of slag provided a self-healing furnace lining minimizing migration of residual ferrosilicon to the shell and production of hot spots. Addition of cooling to the shell improved this issue and extended the life of the furnace.

Commercial Operation

Work on the magnetherm process moved from Beaudean to Marignac France. In 1964 the first commercial scale furnace was brought on line. It had a power supply rated at 2.3 Megawatts and produced 3,400 kg of magnesium per 24 hour cycle.[6] The next generation furnace was installed in 1970. The power input was increased to 4.5 megawatts and a daily production of 7,500 kg per furnace day was achieved. About 1970, Alcoa acquired a license from Pechiney to produce magnesium via the magnetherm process at Addy, Washington.

Northwest Alloys Operation

In 1976, magnethermic furnace operations began. By 1977, nine furnaces were in operation.[7,8] These furnaces had the potential of supplying 8 megawatts of power. The operating pressure was 35 torr. A pellet formed from alumina and dolime was attempted. The idea was to feed hot pellets of alumina-dolime from the kiln to the furnace along with a separate hot dolime feed. This was altered to using hot alumina-lime calcined pellets feed via one feed tank and all the dolime being provided as a separate feed material through another feed tank. The targeted operating cycle time was intended to be 21 hours but owing to operating difficulties the cycle was 24 hours and the production rate was only 7,500 Kg per furnace per day.

The formative years of the 1980's realized the following advantages:

- Corrosion resistance and crack resistance of a stainless steel furnace shell;
- Inflatable gaskets on the slag tapping doors and the furnace tuyere;
- Development of a jacking car for the elbow assembly to allow quick alignment and connection of the elbow assembly to the furnace;
- Development of the motorized slag plugging machine which allowed for more positive assurance that a slag tap would be stopped and a good clay plug achieved each time a slag tap was made;
- Improved welding techniques reduced the difficulties with air leaks in assembled components and especially with center electrodes head and shaft repairs;
- Redesign of the elbow cleaning room to improved safety cleaning efficiency and fume capture;
- Washing and bake-out of elbow parts improved operational reliability of these components;
- Design and implementation of a track mounted jack hammer to provide better cleaning of elbow components;
- Furnace operating pressure changed from 35 to 70 torr;
- Improved computer control algorithms;
- Work was also performed evaluating aluminum as a reductant. [9, 10]

Other feed materials were also improved:

- Ferrosilicon lump was altered to granulated ferrosilicon, Gransil;
- Dead burned magnesite was used to enrich the MgO content of the feed;
- Hard-burned dolime was evaluated as a replacement for regular dolime feed.

By 1989 operations had improved and the cycle time was reduced to 18 hours. Raw material feed quality was improved to decrease the amount of dusty material fed to the furnace and resulted in improved furnace condenser operations. However, to take advantage of these improvements higher feed rates were required which required more power. The increase power requirements caused center electrode life to drop from 28 days to as little as 10 days in some instances. Pressure surges within the furnace caused by feed material piling on the slag and variations in feed material feed rates caused magnesium vapor to migrate into the feed port area and plug the feedport. These necessitated periodic shut downs mid cycle for cleaning, further contaminating of the condenser surfaces. By increasing the liquid portion of the two phase slag, an active slag surface resulted thus reducing the frequency of this problem

<u>Status Prior to Curtailment</u>
Furnace cycle time was reduced from 18 hours to 12 hours with the potential of a 10 hour cycle as a consequence of incremental improvements in the operation and equipment.

Furnace power increased via installation of higher voltage and higher ampere transformers. In actuality, only a little over 12 megawatts were available for use due to: high slag resistivity at the start; low slag resistivity at the end of operations; and condenser limitations. The high performance transformers did have the advantage of allowing high voltage usage at the start of a run to establish good operations and the use of high ampere near the end of each half cycle to maintain good material feed rates at the end of each half cycle when the resistivity would drop significantly due to high slag levels in the furnace. If the raw material feed rate were increased to the point that the secondary condenser on the top of the elbow was condensing a great deal of liquid magnesium, the drain for the secondary condenser, which also acted as the outlet for non-condensable gas could become momentarily vapor locked. If this occurred, the feed system would be blocked with magnesium vapor being forced up the feed port area. Work was underway on a revised condenser design to alleviate the problem.

The premature electrode failure occurred due to three mechanisms of failure:

1. Damage to the electrode flange due to arcing resulting in air leak at the flange perimeter gasket.
2. Erosion of the shaft and head of the copper electrode leading to water leakage into the furnace.
3. Electrode head failures due to excessive power.

These problems were partially addressed with: improved construction materials and design around the electrode flange; establishing low chloride standard for feed materials; iron cladding on the electrode shaft; increased water cooling for the electrode; use of larger diameter electrode heads to allow original current density levels to be reestablished. Electrode life continued to be a significant problem and a significant safety concern up to curtailment.

A major improvement was achieved by addressing the quality of the raw materials used as feed to the reduction furnaces. Initially a soft-burn dolime, alumina-lime pellet, and lump ferrosilicon were used as feed materials. These were replaced with hardburned dolime, dead-burned magnesite, aluminum shot (deox), and Gransil. The purchased materials (Gransil, deox, and dead-burned magnesite) were greatly improved through tightening of material specification and inspection throughout the delivery chain. Thus ensuring no contamination occurred through storage and handling and that material specifications were met. The materials were closely monitored up to the point of actual usage by the furnace.

Kiln performance was improved by changing the procedure used to feed the material from the stockpile. Blending the outside of a stockpile (naturally coarse by gravity segregation) with the interior of another stockpile (naturally fine by gravity segregation) the variation in particle size distribution was reduced and the porosity of the preheater stabilized.

The dolime kiln refractory was revised to allow operation at higher temperatures (1450 C – 1470 C) to produce hardburned dolime. Use of this material greatly reduced magnesium furnace pressure spikes and feedport blockages resulting in an immediate improvement in furnace uptime and overall metal recovery. Dolime samples taken from the kiln were monitored for product quality using nitrogen BET evaluation. Acceptable hardburned dolime was set at equal to or less than 1 square meter per gram with a desired value of 0.7 square meters/gram. Unacceptable dolime was scrapped.

Increasing the amount of magnesium oxide fed per hour improved not only the productivity but also appeared to increase the uniformity of furnace operations. The amount of aluminum shot fed per hour was increased to the point that a separate alumina addition was no longer needed. It was now possible to charge dead burned magnesite to the furnace along with hardburned dolime. The percentage of magnesite to dolime was started at 6% by mass but was steadily increased to 12%. Higher levels were under test at the time of curtailment.

The increased density of magnesium vapor emanating from the furnace appeared to improve the pressure gradient throughout the system. To maximize production, efforts were made to improve the condenser capacity. The crucible surface area was increased and elbow components were thoroughly cleaned after each major. Work was begun on a new secondary condenser elbow design providing a higher surface area for the secondary condenser which would allow more liquid magnesium to return to the crucible without causing backpressure problems in furnace operations.

A significant step in attaining process stability was achieved through revision of the process control algorithm. Initially a predictive approach was used to set the raw material feed ratios for each cycle. It was found that small changes based on feedback, the performance of the furnace over previous cycles, increased furnace stability and productivity.

The equipment used to clean the furnace tuyere opening at each major was significantly changed. In place of manual cleaning of the tuyere with jackhammers, a rotary cleaner with a carbide tipped head devised from a mining/tunnel boring machine was used. This quickly removed any residue decreasing the tuyere opening, while improving working conditions for the furnace attendants and reducing furnace operator exertion and exposure. It also reduced the thermal stresses on the furnace and provided a uniform standard size exhaust opening.

The feed port was completely redesigned. The simple inlet was converted to a double wall port that mechanically opened up and allowed removal of the inner liner. At the end of each cycle a clean feed port liner was inserted into the furnace thus maintaining the maximum opening for feed material on the next cycle and improving operator safety conditions through less exposure to blowbacks from the furnace.

Vacuum leak detection was also improved. A tool was found that allowed the furnace system to be monitored while in operation. It was a very sensitive directional microphone and amplifier. By pointing it at a portion of the furnace, a telltale hiss could be heard if there was a vacuum leak. This could then be verified by pressure testing at the end of a cycle. Adoption of this tool increased furnace up time and decreased loss of product due to re-oxidation in the furnace.

In an effort to increase production through more uniform furnace and condenser operation two programs were initiated: 1) liquid phase operation capable of vacuum or atmospheric operation and 2) plasma furnace operation at atmospheric pressure. Both were terminated before successful results were achieved.

Pechiney operated a commercial liquid phase condenser for a number of months under vacuum conditions. [11]

Mintek operated a test furnace and liquid phase splash condenser at or near atmospheric conditions. The reduction furnace used a DC plasma power supply with a movable electrode. By operating at a higher temperature, they were able to successfully demonstrate the production of magnesium at atmospheric conditions using a DC plasma furnace coupled with a splash condenser. The reported results were published Oct. 2006 by M. Abdellatif of Mintek.[12]

## Conclusion

A number of improvements were made from 1964 to curtailment in 2001. While these changes improved operations and productivity, market forces dictated closure in 2001.

This paper mentions only a few of the things accomplished by the people at NWA, Alcoa, and our technological associates in France. These improvements allowed this plant to establish itself and to meet the rigorous environment requirements placed upon this organization. Significant changes were made from the initial concept furnace to the 12 Megawatt production furnace used at the turn of the century. These changes resulted in substantial productivity and efficiency gains, significant process improvements, major safety improvements, and environmental gains. Many more milestone improvements could have been attained if operations had continued.

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