Improving the Electrolytic Process for Magnesium Production

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Magnesium Corporation of America has completed a development program designed to improve the performance efficiency of the electrolysis system and eliminate operating chlorine losses. This work has culminated in the recent modernization of the process. The conversion has provided a number of operating benefits including significant reductions in labor costs, energy costs, maintenance costs, and environmental releases. This paper will review the development, design, environmental impact, and cost benefit of the project.

INTRODUCTION

MagCorp, the oldest primary magnesium producer in the United States, has operated electrolytic processes for 30 years. At its Utah production facility, the Great Salt Lake provides unique advantages in preparing of $MgCl_2$ for electrolysis. The MagCorp production process uses the anhydrous magnesium-chloride preparation method, which was developed through a combination of pilot plant data and empirical optimization. Using solar recovery of brine from the Great Salt Lake, a pure magnesium-chloride brine is collected at a low cost. After several chemical treatment steps, $MgSO_4$ is converted and boron impurities removed. The purified brine is then flash-dried to remove the majority of water before the material is carbo-chlorinated to eliminate all residual oxygen content.

The carbo-chlorination process produces a molten magnesium-chloride feedstock for use in several types of monopolar electrolyzers that have been installed in the Rowley facility. These designs include magnesium cells with and without diaphragms. The major products from the electrolysis area include chlorine gas, which is reused in the process or sold, and magnesium metal, which is vacuum harvested and directed to the casting plant. Recovered metal is refined, alloyed, and cast into more than 30 different product lines, including direct chilled billet.

The low cost of magnesium-chloride production and the flexibility of the facility casting system have contributed to the ongoing success of the process. The use of older electrolysis technology, however, has led to increased labor and energy expenses, along with increased environmental losses of chlorine. To resolve the problems, the company has modernized its electrolysis process, improving efficiency and reducing costs.

MODERNIZATION OBJECTIVES

A modernization program was initiated six years ago to improve production efficiency and to eliminate environmental chlorine issues at the facility. This technical project had two distinct components: the improvement of magnesium-chloride cell feed purity and improvement of electrolyzer performance. The feed-purity project was directed toward the cost-effective reduction of oxygen, iron, and carbon in the $MgCl_2$ cell feed. The electrolysis project involved designing and evaluating various electrolyzer concepts that would reduce energy consumption, eliminate chlorine losses, and require less operating labor.

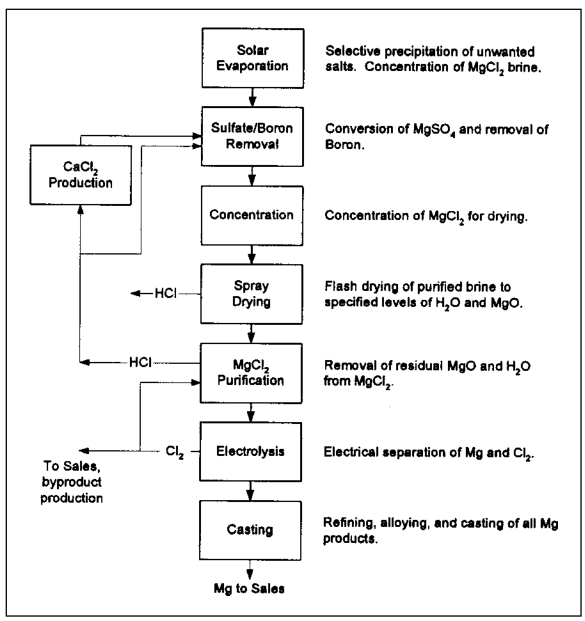

Figure 1. MagCorp process flow sheet.

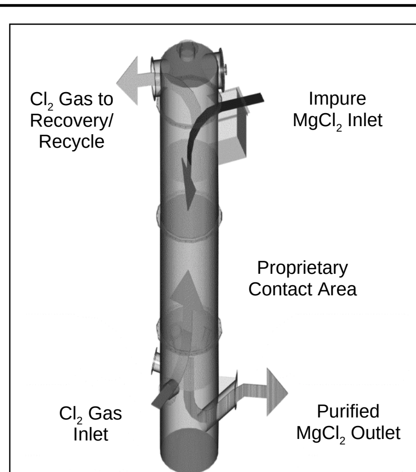

Figure 2. A tertiary $MgCl_2$ chlorinator.

The technical objectives would need to be carried out in a brownfield installation with minimal interruption to ongoing magnesium production. The cost of the project would need to be significantly more favorable than a greenfield project.

SYSTEM DEVELOPMENT

Development of the feed-purity project included a thorough review of the options available to meet the objectives. The existing MagCorp process utilizes continuous magnesium-chloride chlorinators with a high throughput capacity. This productivity is realized through the use of proper reactant control as well as iron-chloride reaction intermediates. Elimination of the residual carbon and iron from the reaction has been a major technical obstacle. Work that began in 1996 to determine the best methods to remove these impurities culminated in the addition of a chlorination component to the process. This chlorination step utilized a proprietary technique of vertical chlorination, which was found to be efficient from both a cost and a process perspective.

The electrolysis project began with a review of available technical options. Eleven different electrolyzer concepts were tested over a three-year period before a final design was chosen. The selection criteria included overall performance, operating simplicity, ruggedness, and projected maintenance costs.

$MgCl_2$ PURIFICATION PROJECT

The electrolytic production of magnesium is a complex process that can be simplified into two major steps: preparation of magnesium chloride and the subsequent electrolysis of the salt. Preparation of magnesium chloride is the key to successful electrolysis and all magnesium electrolyzers must be designed to handle the specific capabilities of the feed-preparation step. Magnesium-chloride purity at MagCorp has historically averaged 0.70% non-electrolyte impurities, which is significantly higher than the 0.20% maximum designed for most high-efficiency electrolyzers. The technical objective required significant impurity removal with minimal changes in infrastructure.

The original MagCorp chlorination system utilizes refractory lined cells arranged in a primary and secondary process scheme. These units utilize chlorine sparging tubes to introduce gas into the reactors. Process kinetics are driven by reactant control, reactant contact (control of chlorine vapor bubble size), residence time, and mixing. The modified system would require the following changes:

- Process modifications for improved impurity removal
- Upgraded control system to optimize reaction kinetics
- Improved product surge handling and purity control
- Improved design of existing chlorinators to optimize performance
- Improved feed delivery system to the electrolyzers

Significant process testing resulted in the decision to add tertiary chlorination to the system. This involved installation of a proprietary vertical chlorinator to remove residual oxygen and iron. The chlorinator was designed using standard contactor hydraulics and was modified through pilot testing.

Construction materials were optimized through thorough field testing. The final product incorporated a rugged design with appropriate gas introduction, liquid distribution (molten $MgCl_2$), efficient contactor area, and appropriate offgas handling for recycling the high-strength chlorine exiting the column.

Existing chlorination equipment was upgraded with the installation of an electronic control scheme for reactant, power, and gas handling. The chlorinators were modified to accept a vertical electrode design (vs. horizontal), which provided an opportunity to improve the refractory

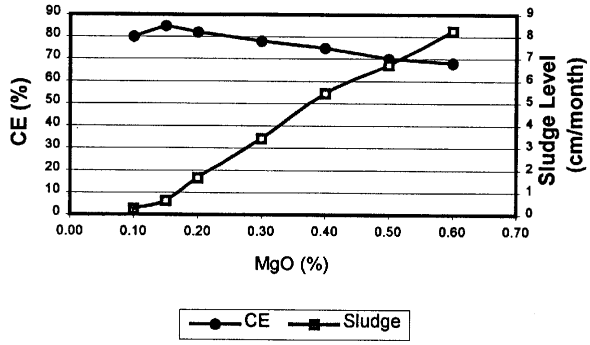

Figure 3. Cell feed MgO vs. CE/sludge.

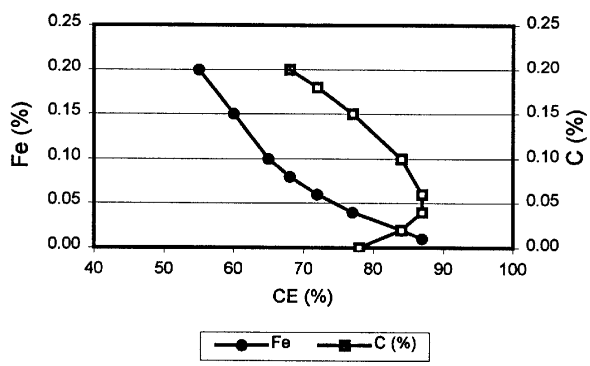

Figure 4. Cell CE vs. cell feed Fe/C.

layout. The chlorinators were also altered to eliminate air introduction into the reactors. These modifications dramatically improved reliability, cleanliness, and control of the system.

Equipment modifications downstream of the tertiary chlorination step included additional product surge capacity and new mobile feed hauling equipment to transport $MgCl_2$ to the cell rooms. The surge units provided significant capacity within a controlled environment to maintain $MgCl_2$ purity. These units also incorporated equipment designed to provide precipitative removal of carbon and other impurities.

The magnesium-chloride delivery sys-

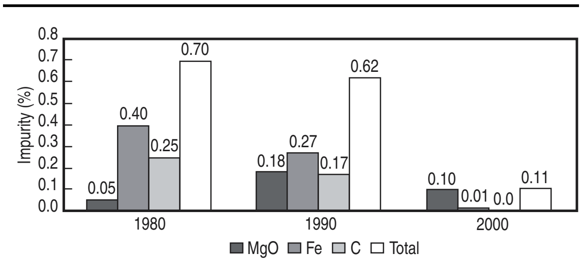

Figure 5. Historical cell feed impurity levels.

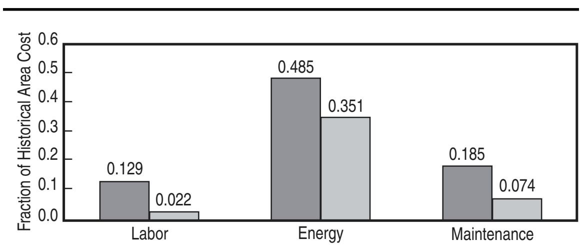

Figure 6. Historical vs. modernized costs.

tem to the electrolyzers required replacement of the existing mobile equipment fleet. The new units incorporated static suction-line technology and much larger capacity (11.5 tonne vs. 3.2 tonne). These modifications resulted in a substantial reduction in the increase of $MgCl_2$ impurities due to handling. The old transport system observed an average impurity increase of 500 ppm compared to 100 ppm with the new system.

CELL FEED PERFORMANCE

Impurities in magnesium-chloride feed reduce the efficiency of electrolysis. The effects of these impurities (MgO, Fe, and C in the MagCorp system) have been studied and discussed in a number of literature sources. The interaction of these components with magnesium metal collection and their effect on direct current (DC) cell electrode surfaces has been accurately reviewed by Strelets.[1] Figures 3–4 illustrate the effects of these components in the electrolysis area as measured in the MagCorp system.

Product purity improved significantly with modifications to the $MgCl_2$ feed-preparation process, while operating costs decreased by 10%. Figure 5 illustrates the results of feed-preparation technology improvements at the facility, where high-quality magnesium-chloride cell feed is produced for less than $0.056/kg.

MAGNESIUM ELECTROLYSIS PROJECT

Due to the labor, energy, and rebuild expenses associated with the equipment, magnesium electrolysis is the most cost-intensive processing step in the electrolytic method of production. Vast amounts of information are available detailing theoretical and practical designs of magnesium electrolyzers, including monopolar diaphragm units, monopolar diaphragmless units, and multipolar units. All of these electrolyzers can be designed to operate at various power levels and interelectrode distances. Small design changes can induce significant differences in cell performance and can significantly alter cell-feed purity requirements.

MagCorp, which operated monopolar diaphragm electrolyzers (IG Farben based) for 25 years, realized increased productivity and improved chlorine-collection capability when it installed a diaphragmless electro-

Table I. MagCorp Electrolyzer Comparison

Item	Diaphragm Cell	Diaphragmless Cell	M Cell
Operating Temperature	704–760°C	704–760°C	676–704°C
Chlorine Strength	70%	80%	>96%
Chlorine Recovery	85%	98%	99.9%
Power Efficiency (Min/Max) kwh/kg	18.8 to 19.9	16.6 to 18.8	12.1 to 14.3
Voltage	6.5 to 7.0	6.0 to 6.3	4.5 to 5.0
Production (Max)	1.0 t/d	1.4 t/d	2.8 t/d
Melt Capacity	20 t	42 t	91 t

Table II. Comparison of Industrial DC Cells*

Company	Cell	Cell Type	Power Voltage	Unit Efficiency	Production
Norsk-Hydro[2]	DLE	Monopolar	5.3 V	13.0 kwh/kg	>4.0 t/d
Alcan Int.[3]	MP3	Multipolar	NA	10.5 kwh/kg	NA
MagCorp[3]	M-Cell	Monopolar	5.0 V	12.6 kwh/kg	2.8 t/d
AVISMA[4]	Bottom Entry	Monopolar	4.7 V	13.5 kwh/kg	0.7 t/d
UKTMP (Kaz)[4]	Top Entry	Monopolar	4.8 V	13.2 kwh/kg	1.8 t/d

*Competitor information was derived from published reports and the basis of evaluation in each category may be inconsistent.

lyzer at the facility in the 1980s. Disadvantages of early electrolyzer designs include excess labor requirements, unfavorable chlorine recovery, and limited unit productivity. A new electrolyzer would be designed to provide the following:

- Compatibility with improved $MgCl_2$ feed
- A 30% reduction in energy consumption
- A 300% productivity improvement
- A significant reduction in labor and maintenance requirements
- Improved environmental and hygiene performance
- Ability to absorb process upsets

The new electrolyzers, referred to as M cells, are large-scale, monopolar diaphragmless electrolyzers. These units utilize large electrodes, a reduced inter-electrode distance (less than 30 mm), and channeled magnesium collection. Significant development work was required to optimize the performance relationship between current density, electrode geometry, electrode gap, magnesium collector arrangement, cell thermal balance, and overall current efficiency. The final design concept is an advanced version of the successful diaphragmless electrolyzer. The design modifications used on the M cell system resulted in the following advantages:

- No requirement for control of cell electrolyte level
- No requirement to replace graphite anodes
- No requirement to desludge the units
- Greater than 99.9% collection of chlorine
- No requirement for cell heat exchanger or alternating current heating system
- Improved chlorine compartment integrity

A comparison of the historical performances of the major MagCorp electrolyzer designs is shown in Table I.

The impact of the new cell design to the MagCorp electrolysis system has been significant. The technical challenge of installing an advanced electrolyzer in an existing facility was overcome with minimal process interruption. The key elements involved in the project included the following:

- *Electrical System*—The electrolyzer DC power system was replaced with new rectifier and busbar capacity, which allowed cell power delivery of more than 300 KA. The high-efficiency busbar, coupled with the new electrolyzer design, resulted in improved power efficiencies. Actual performance levels of 13.31 kwh/kg Mg (including all busbar) have been demonstrated at the plant site, with in-cell power consumption averaging 12.52 kwh/kg Mg. The electrical performance of the system is expected to improve with additional experience.
- *Labor Utilization*—The increased scale of the M cell system has provided a framework for reduced operating labor. Older MagCorp electrolyzers provide 1.0 to 1.4 tonnes of magnesium per unit day. The M cells produce up to 2.8 tonnes of magnesium per day, which significantly reduces the number of operating units. This change, in conjunction with the improved feed delivery system, has reduced area labor requirements by 83%.
- *Maintenance*—Maintenance costs of the M cell system are dramatically improved from older electrolyzer designs. This is due to the design ruggedness, design simplicity, and an improved electrode cooling system. Maintenance requirements have been reduced 60%. At less than $0.11/kg Mg, cell-rebuild expenses associated with the M cells are competitive with advanced cell designs in other operations.
- *Environmental*—Environmental emissions have greatly improved, as has work-place hygiene. Worker exposure to both chlorine and cell thermal emissions have been reduced 45% and 30%, respectively. Chlorine collection has improved significantly, with greater than 99.9% capture due to the proprietary metal collection system. The strength of the generated chlorine is exceptional (greater than 96%), which improves the economy of downstream gas cleaning and recycling.

A number of considerations are utilized in selecting electrolyzer designs, including performance, operating simplicity, and process ruggedness. These factors vary somewhat by individual industrial site, and have a significant impact on the overall economics of electrolyzer performance. Selected performance comparisons of magnesium electrolyzers are presented in Table II.

CONCLUSIONS

The successful modernization of the MagCorp electrolysis system required several years of development and extensive technical support. The result has been a 20% reduction in overall production costs. The installed cost of the MagCorp feed purification system and electrolysis upgrade was $1,200 per tonne of annual magnesium production, which compares favorably to the $3,000 to $15,000 per tonne of greenfield capacity reported by various Eastern and Western organizations.

The installation of this system has demonstrated that it is technically feasible to retrofit existing production facilities with equipment that provides excellent results. The significant benefits of this approach can provide older producers with the efficiencies required to compete in the high-quality magnesium market with reasonable rates of return on facility investments. The technological approach can also provide the framework for significant volume expansions should the need arise due to future market growth.

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