

# **NEW MAGNESIUM – ENHANCED LIME FLUE GAS DESULFURIZATION PROCESS**

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## **ABSTRACT**

Carmeuse North America has developed a new magnesium-enhanced-lime-based wet flue gas desulfurization (FGD) process for control of sulfur dioxide emissions. This process is an improvement upon an older magnesium-enhanced lime process, which has been in use in the USA since 1977. The magnesium-enhanced lime process utilizes 2.25 million metric tons of lime annually. Since the year 2000, 27% of this lime is utilized in an improved version of the process that produces valuable by-products, gypsum and magnesium hydroxide. While the by-product produced by the old process (calcium sulfite) had no use and had to be disposed in landfills, gypsum produced by the new process is sold for manufacture of building materials such as wallboard and plaster. Magnesium hydroxide produced by the new process can be used for control of a second pollutant, sulfuric acid mist. The new process can also produce magnesium hydroxide as a byproduct, which has been used successfully for control of sulfuric acid emissions and to eliminate plume opacity.

This paper gives background on use of magnesium-enhanced lime-based FGD in the USA, identifies installations using this process, describes the process, describes beneficial use of by-product magnesium hydroxide, and compares economics with competing processes. This process can obtain SO<sub>2</sub> removal efficiency of 99% while scrubbing flue gas from burning high-sulfur fuel, which is characteristic of magnesium-lime based scrubbing. The process produces gypsum of 99% purity and achieves lime utilization of 99.9%.

## **INTRODUCTION**

Lime is used extensively in the USA for removal of sulfur dioxide (SO<sub>2</sub>) from flue gases produced by burning of sulfur-containing fossil fuels at power plants and industrial facilities. Table 1 shows major categories of lime used in the USA in 2000<sup>1</sup>. Lime used for removal of SO<sub>2</sub> amounts to 3.16 million metric tons per year or 16% of lime used.

**Table 1: Uses of Lime in the USA**

Use	Metric tons lime per year	Percentage
Steel	6150000	32
Chemical and Industrial	4670000	24
Flue Gas Desulfurization	3160000	16
Construction	2070000	11
Other Environmental	1960000	10
Non-ferrous metals	1310000	7
Total	19320000	

Two major types of lime-based FGD processes are used in the USA: “dry lime” and “wet lime” processes. Dry lime processes include dry injection, spray dryer or semi-dry processes, and circulating fluid bed processes, such as developed by the German company Lurgi. Wet lime processes include the wet high-calcium lime process and the magnesium-enhanced lime process. Table 2 shows the major types of lime-based FGD in the USA and the tons of lime used annually by each process<sup>2</sup>. The magnesium-enhanced lime process utilizes 71% of FGD lime, or 2.25 million metric tons per year.

**Table 2: Lime-based FGD Processes in the USA**

Process	Metric tons lime per year	Percentage
Wet magnesium-enhanced	2250000	71
Wet high-calcium	400000	13
Dry	510000	16

Table 3 shows use of all types of FGD processes in the USA, including lime-based processes, by MW of power generation served<sup>3</sup>. The magnesium-enhanced lime process serves 15783 MW or 17% of FGD capacity. Lime-based processes compete with the wet limestone process, which serves 56642 MW, or 59% of FGD capacity.

**Table 3: FGD Processes Used in the USA**

Process	MW Served	Percentage
Wet limestone	56642	59.4
Wet (high-calcium) lime	7111	7.5
Wet magnesium-enhanced lime	15783	16.6
Dry/semi-dry lime	6221	6.5
Other	9522	10.0
Total	95279	100.0

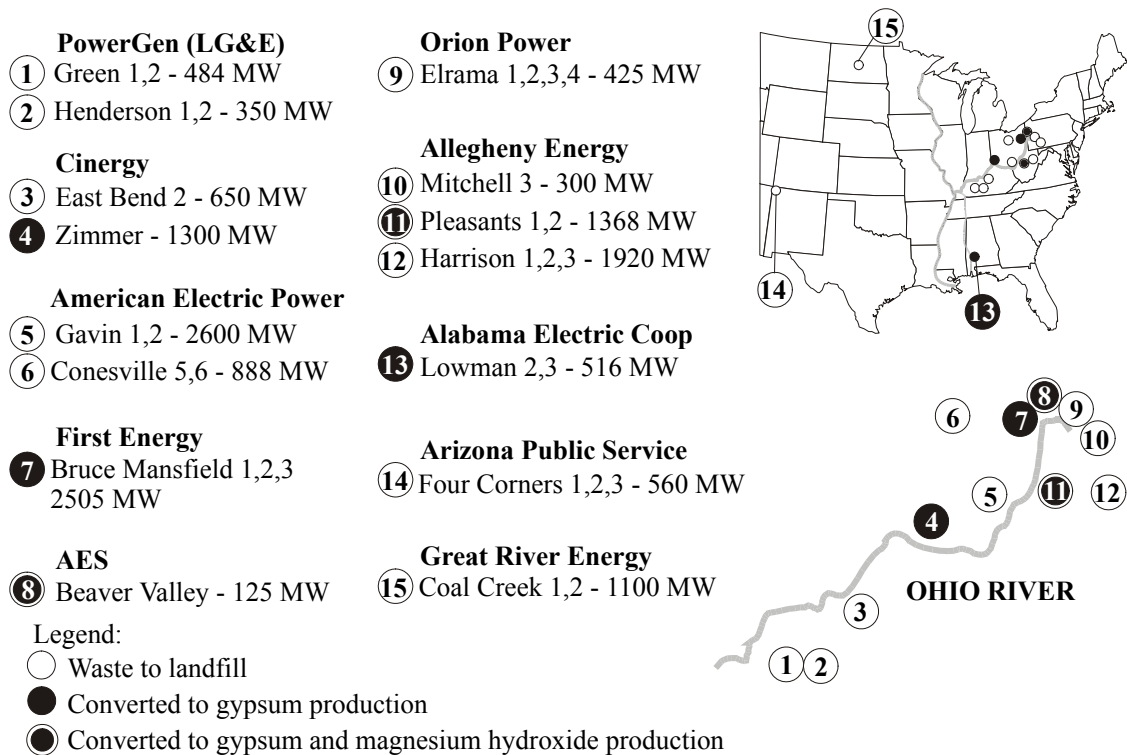
## EVOLUTION OF THE MAGNESIUM-ENHANCED LIME PROCESS

The magnesium-enhanced lime process was first installed in 1976. Its use grew in the 1980's as new coal-fired power plants were installed in the eastern part of the USA, especially along the Ohio River. These plants required installation of FGD for control of SO<sub>2</sub> emissions to comply with the 1970 federal Clean Air Act. The magnesium-enhanced lime process was selected for these plants based on its ability to achieve more than 90% removal of SO<sub>2</sub> generated from burning high-sulfur coals, ease of operation, and deposit-free absorber operation.

The second period of growth in magnesium-enhanced lime FGD occurred in 1995, when selected existing power plants were retrofitted with FGD to comply with 1990 revisions to the Clean Air Act. The magnesium-enhanced lime process was selected by 4700 MW of generating capacity. SO<sub>2</sub> removal in these systems ranged from 95% to 98%, the highest removal ever guaranteed in the USA.

Magnesium-enhanced lime process installations serve a total of 15743 MW of generating capacity. These installations are shown in Figure 1.

**Figure 1: Installations of the Magnesium-enhanced Lime Process**



Up to 1995, all of the magnesium-enhanced lime systems produced a solid waste by-product, calcium sulfite hemihydrate, that had no value and had to be disposed in landfills. Dravo Lime Company began work in 1997 (Carmeuse acquired Dravo in

1998) to convert some of its customers FGD system to ones that produced valuable by-products, calcium sulfate dihydrate, or gypsum, and magnesium hydroxide, using technology developed in the previous decade by Dravo. Eliminating disposal in landfills substantially reduces operating costs, and gypsum can be sold to building material companies for production of wallboard, or sold to cement manufacturers for use as a set retardant. Wallboard manufacturers that utilize the gypsum by-product include Lafarge, US Gypsum Co., and National Gypsum Co. Flyash that had previously been needed for mixing with calcium sulfite prior to landfills can instead be sold for concrete manufacture.

Two of the converted stations also produce byproduct magnesium hydroxide  $[\text{Mg}(\text{OH})_2]$ . The byproduct  $\text{Mg}(\text{OH})_2$  can be used for wastewater treatment and for control of sulfuric acid emissions, discussed in more detail below.

From 1997 to 2000, 4300 MW, about 27% of magnesium-enhanced lime capacity was converted to the new process. These conversions are described in detail in earlier papers<sup>4,5,6</sup>.

### **DESCRIPTION OF THE MAGNESIUM-ENHANCED LIME PROCESS**

The magnesium-enhanced process uses lime that has 3-6 weight percent magnesium oxide ( $\text{MgO}$ ) with the balance calcium oxide.  $\text{MgO}$  in the lime produces magnesium sulfite ( $\text{MgSO}_3$ ) in absorber liquid.

Magnesium sulfite acts as a catalyst to greatly increase  $\text{SO}_2$  capture efficiency. Magnesium sulfite is a soluble salt, and it accumulates in the liquid portion of the slurry. Magnesium sulfite is also an alkaline salt, so it is able to react with acid and prevent a large drop in pH in liquid in contact with flue gas. Preventing a large drop in pH in liquid sprayed into the gas to absorb  $\text{SO}_2$  greatly reduces resistance to transfer of  $\text{SO}_2$  from the gas to the liquid, which in turn greatly increases  $\text{SO}_2$  capture efficiency<sup>7</sup>.

Magnesium sulfite also prevents calcium-based deposits from forming on the insides of the absorber. The presence of magnesium sulfite in the slurry liquid depresses the concentration of calcium compounds like calcium sulfate (gypsum) in the liquid. In the absence of magnesium sulfite, accumulation of gypsum on the walls of the absorber and on piping is common.

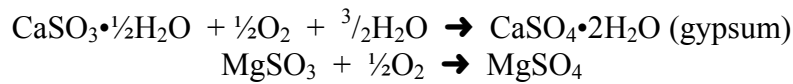
### **Absorption of $\text{SO}_2$**

Absorption of  $\text{SO}_2$  in the new magnesium-enhanced process is the same as in the old process. Figure 2 shows absorption of  $\text{SO}_2$  using the magnesium-enhanced process. Lime containing 3-6 weight percent  $\text{MgO}$  is slaked and then added to a reservoir of slurry (reaction tank) at the bottom of an absorption tower to maintain pH of the slurry at 6. The slurry consists of the products of reaction of lime with  $\text{SO}_2$ : solid calcium sulfite hemihydrate and a liquid phase containing magnesium sulfite. Slurry from the reaction tank is pumped through nozzles and sprayed into the flue gas.  $\text{SO}_2$  reacts with  $\text{MgSO}_3$  to form magnesium bisulfite  $[\text{Mg}(\text{HSO}_3)_2]$  and is absorbed by

liquid in the slurry droplets. The slurry then falls into the reaction tank. Slaked lime containing both calcium hydroxide [Ca(OH)<sub>2</sub>] and magnesium hydroxide [Mg(OH)<sub>2</sub>] reacts with magnesium bisulfite to precipitate solid calcium sulfite hemihydrate (CaSO<sub>3</sub>•½H<sub>2</sub>O) and regenerate MgSO<sub>3</sub>. MgSO<sub>3</sub> is then available for continued capture of SO<sub>2</sub> when the reaction tank slurry is recirculated.

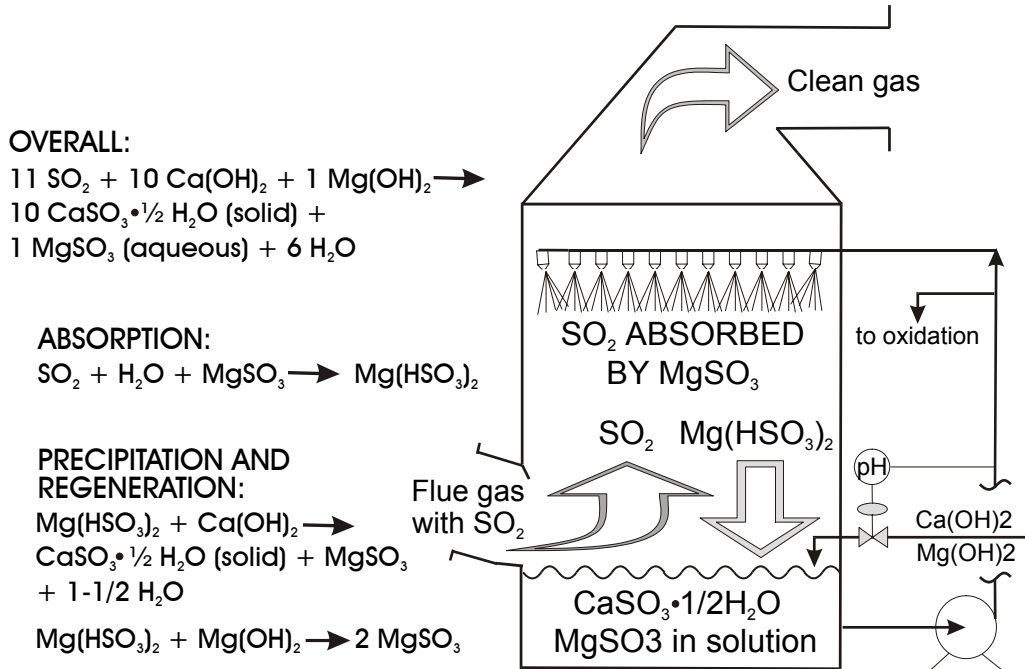
**Production of By-products**

Figure 3 shows a flow diagram of the entire magnesium-enhanced lime process. A portion of absorber slurry, containing solid calcium sulfite hemihydrate and soluble magnesium sulfite, flows to an oxidation tower. Compressed air flows into the bottom of the tower. Calcium sulfite hemihydrate is converted to calcium sulfate dihydrate, or gypsum, and magnesium sulfite is converted to magnesium sulfate:

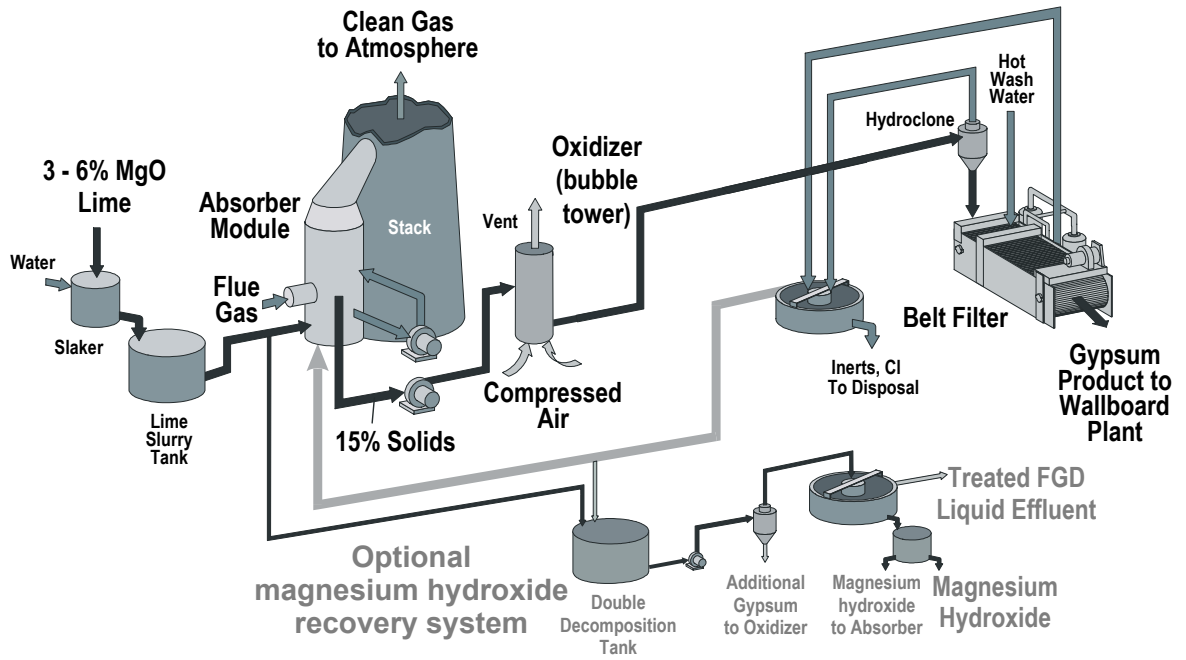


Gypsum is recovered by filtration and is shipped to either a wallboard manufacturer or a cement manufacturer. Most of the liquid is returned to the absorber, while a portion of the liquid is withdrawn. This withdrawn liquid, containing MgSO<sub>4</sub>, is available for production of magnesium hydroxide as a second by-product.

**Figure 2: SO<sub>2</sub> Absorption in Magnesium-enhanced Lime Process**



**Figure 3: Magnesium-enhanced Lime Process with Optional Magnesium Hydroxide Recovery**



**Production Of By-Product Magnesium Hydroxide**

Magnesium hydroxide is produced by adding slaked lime to the liquid, containing MgSO<sub>4</sub>, that is withdrawn from the FGD system. Chloride ions (Cl<sup>-</sup>) accumulate in this liquid as magnesium chloride (MgCl<sub>2</sub>) due to absorption of hydrochloric acid from the flue gas along with SO<sub>2</sub>. This liquid contains all of the magnesium that was present as magnesium hydroxide in slaked lime added to the FGD system. MgSO<sub>4</sub> undergoes a double-decomposition reaction with calcium hydroxide to precipitate both magnesium hydroxide and gypsum:



Magnesium hydroxide particles formed are very small, 3 microns average, while the gypsum particles are much larger, 60 microns average.

Magnesium chloride also reacts with calcium hydroxide to precipitate additional magnesium hydroxide:

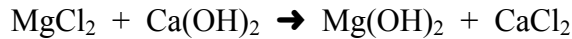
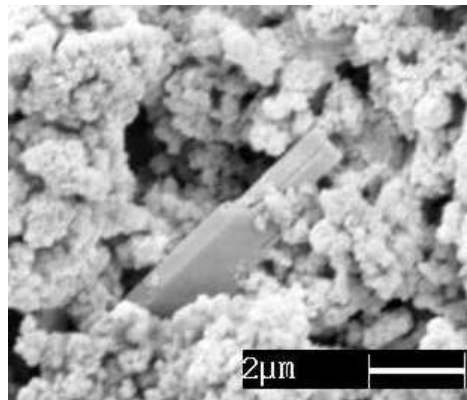


Figure 3 shows equipment used for magnesium hydroxide recovery. The equipment is similar to equipment used for wastewater treatment. It includes a double decomposition tank where lime and withdrawn FGD liquid is reacted, liquid cyclones (hydroclones) for separation of magnesium hydroxide and gypsum particles. Their large size difference allows efficient separation. Separated magnesium hydroxide flows to a thickening tank, where it settles to a slurry containing 18-20% solids. Separated gypsum is returned to the oxidizer, where it becomes part of the main gypsum stream and increases gypsum production.

Figure 4 gives characteristics of recovered by-product Mg(OH)<sub>2</sub>. Note in the scanning electron microscope (SEM) image the fine size of the magnesium hydroxide compared with the gypsum crystal present. The magnesium hydroxide has a very high specific surface area, 55 square meters per gram.

**Figure 4: Analysis and SEM Image of By-Product Magnesium Hydroxide**

Magnesium Hydroxide Chemical Analysis	
MgO as Mg(OH) <sub>2</sub> , wt. %	73
Gypsum as CaSO <sub>4</sub> •2H <sub>2</sub> O, wt. %	21
Inerts, wt. %	6
Total Suspended Solids, %	18
BET Specific Surface Area, m <sup>2</sup> /g	55
Particle Size D50	3 micron



Because precipitation of magnesium hydroxide requires slaked lime, production of by-product magnesium hydroxide increases lime use. For a magnesium-enhanced lime FGD system using lime with 6 weight percent MgO, and assuming 100% recovery, lime use increases by about 9%.

### **USE OF BY-PRODUCT MAGNESIUM HYDROXIDE FOR CONTROL OF SULFURIC ACID EMISSIONS**

When coal containing sulfur is burned, most of the sulfur is converted to sulfur dioxide. A small portion of the sulfur, about 1%, is converted to sulfur trioxide (SO<sub>3</sub>). A second source of sulfur trioxide is equipment used for control of nitrogen oxides [nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>)], called selective catalytic reduction (SCR). In SCR, flue gas is mixed with ammonia and flows over a catalyst, where ammonia reacts with the nitrogen oxide and converts them to harmless nitrogen. An undesirable side reaction occurs which converts 0.5-1.5% of SO<sub>2</sub> in the flue gas to SO<sub>3</sub>. As a result of generation of SO<sub>3</sub> in both the furnace and SCR, up to 2.5% of sulfur in the fuel can be converted to SO<sub>3</sub>. When flue containing SO<sub>3</sub> is cooled to less than about 175°C, the SO<sub>3</sub> reacts with water in the flue gas and condenses as sulfuric acid. If cooling is very fast, such as occurs in a wet scrubber, where the flue gas is cooled to 52°C, the sulfuric acid condenses to a very fine mist, with most of the droplets smaller than 0.5-1 microns. When this mist is emitted into the atmosphere, these sub-micron droplets reflect light, and the plume becomes visible. All power plants have regulatory limits on visible emissions, and the sulfuric acid mist can cause these limits to be exceeded.

By-product magnesium hydroxide has been tested for control of sulfuric acid mist emissions at two large power plants, Bruce Mansfield and Gavin. The magnesium hydroxide was injected into the superheater region of the furnace at a temperature of 925-1200°C, where it reacts with sulfur trioxide (SO<sub>3</sub>) forming inert magnesium sulfate:



The tests showed a 70-90% reduction in sulfuric acid emissions and a large decrease in visible emissions.

Additional benefits of removal of SO<sub>3</sub> in the furnace include reduction in deposits on heat transfer surfaces, especially the air heater, where flue gas is cooled to about 150°C. Removal of 90% of SO<sub>3</sub> from the flue gas with Mg(OH)<sub>2</sub> before the air heater would allow the gas to be cooled to 133°C without condensation of sulfuric acid. This allows greater recovery of heat from the gas and an increase in furnace efficiency of about 1%.

Magnesium hydroxide injection is known to reduce build-up of slag in furnace. Slag is molten ash which can accumulate on superheater tubes.

An additional benefit of magnesium hydroxide recovery is where FGD wastewater treatment is required. All FGD systems produce liquid waste. The wastewater contains

chloride ions as described above and also small amounts of heavy metals removed from the flue gas in the absorber. Treatment of this liquid with lime in the magnesium hydroxide recovery equipment precipitates most of these metals along with the magnesium hydroxide. When the recovery magnesium hydroxide is injected into the furnace for control of SO<sub>3</sub> emissions and reduction in slagging, the heavy metals can be removed with flyash in particulate removal equipment like an electrostatic precipitator.

### **ECONOMICS OF THE MAGNESIUM-ENHANCED LIME PROCESS**

A recent study of capital and operating costs of the major FGD processes, wet limestone, dry lime, and wet magnesium-enhanced lime found that the magnesium-enhanced lime process was cost competitive with the wet limestone process for fuels with a sulfur content of 2% or higher<sup>8</sup>.

FGD costs comparisons are most sensitive to fuel sulfur content and reagent (lime or limestone) costs. Figures 5 and 6 shows results of cost comparisons<sup>9</sup> between the magnesium-enhanced lime process and the wet limestone process for 500 MW FGD systems. Major inputs to the cost comparisons are included in Table 4:

**Table 4: Inputs to FGD Cost Comparison**

<b>Parameter</b>	<b>Mg-enhanced lime</b>	<b>Limestone</b>
Equipment cost, US \$/kW	175	200
Absorber pump recirculation, liters liquid per cubic meter gas	4	12
Power consumption, % of generation	1.3	2.0
By-products	Gypsum, magnesium hydroxide	Gypsum
Reagent cost, US \$/metric ton	55	16.5
Reagent ratio, moles per mole SO <sub>2</sub> absorbed	1.005	1.05

Figure 5 shows wet process costs versus fuel sulfur content. As seen from the figure, the magnesium-enhanced lime process is competitive with the limestone process for high-sulfur fuels over a wide range of fuel sulfur content.

**Figure 5: Effect of Fuel Sulfur Content on FGD Costs**

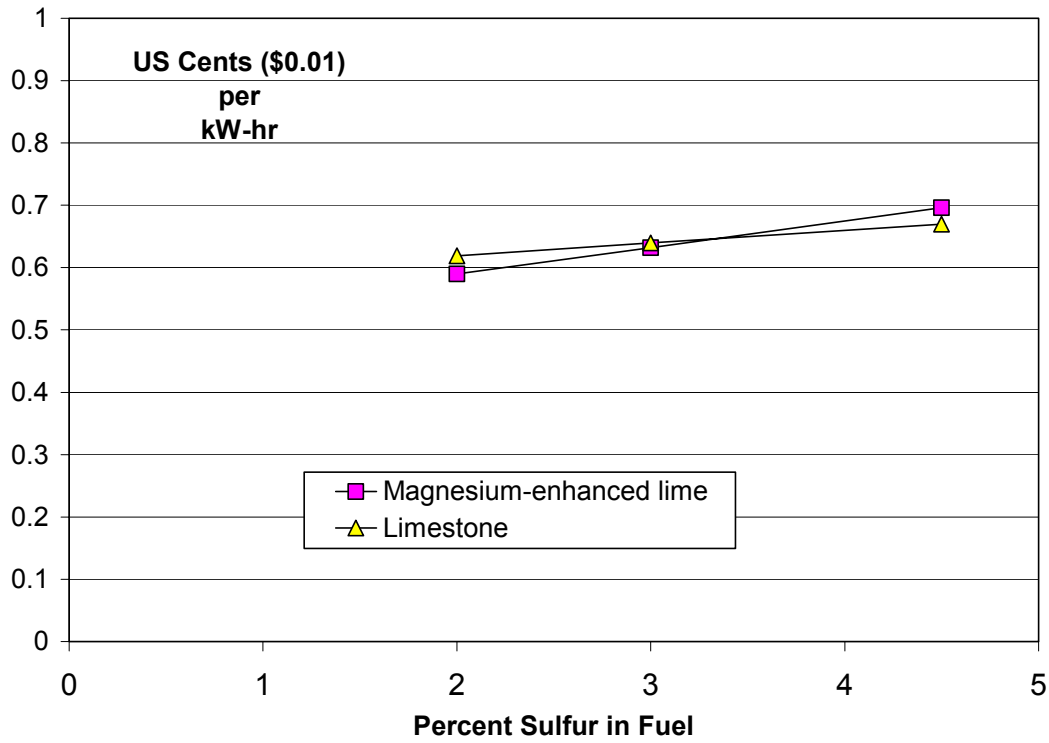


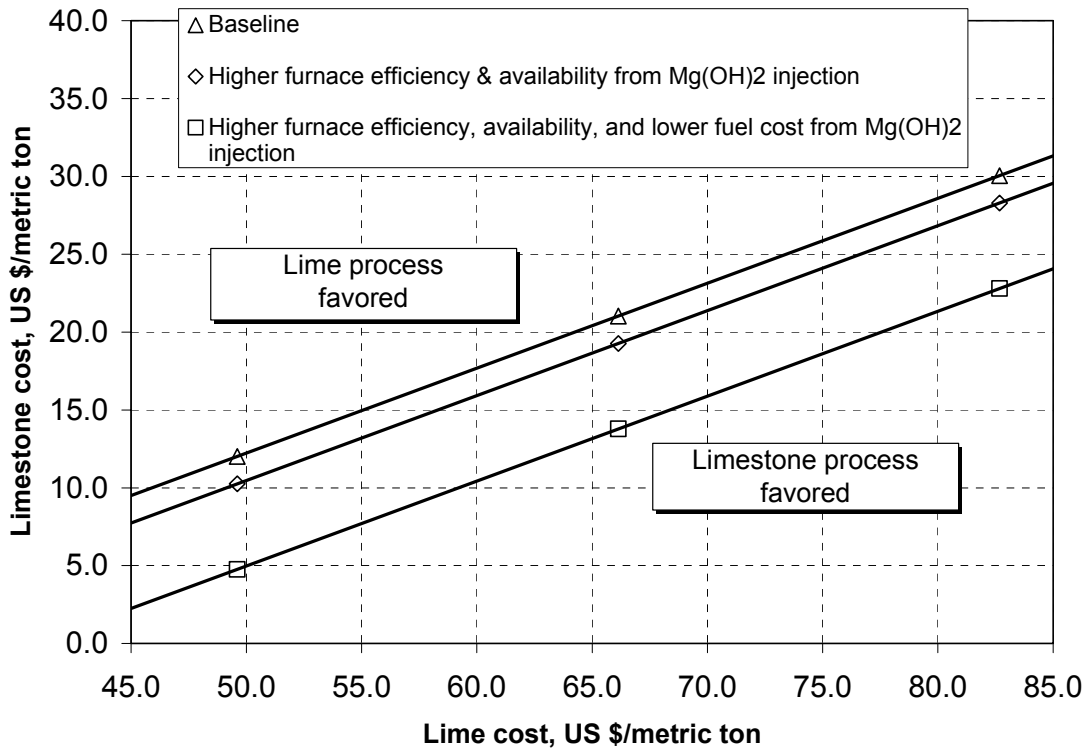
Figure 6 shows the effect of lime and limestone costs on cost competitiveness of the magnesium-enhanced lime process for a fuel sulfur content of 3%. Points on each line represent lime and limestone costs that yield equal overall FGD costs. For each line, the magnesium-enhanced lime process is favored for limestone costs above the line of a given lime cost. For example, for the “baseline” case, a magnesium-enhanced lime installation with a lime cost of \$55/metric ton would have the same overall FGD cost as a wet limestone installation with a limestone cost of \$15/metric ton. So the magnesium-enhanced lime process would be less costly overall for limestone cost above \$15/metric ton.

Additional lines indicate cost benefits achievable with injection of by-product magnesium hydroxide for control of sulfur trioxide and reduction in slag build-up. Cost benefit parameters related to injection of by-product magnesium injection are included in Table 5. The cases in Figure 6 that include benefits from magnesium hydroxide injection show that the magnesium-enhanced lime process is made more competitive.

**Table 5: Additional Inputs to FGD Cost Comparisons in Figure 6**

Parameter	Mg-enhanced lime	Limestone
Furnace efficiency increase due to magnesium hydroxide injection, %	0.75	N/A
Annual increase availability due to magnesium hydroxide injection, hours	48	N/A
Reduction in fuel cost due to magnesium hydroxide injection, \$/metric ton	0.55	N/A

**Figure 6: Break-even Points for FGD Cost Comparisons Including Benefits from By-product Magnesium Hydroxide Injection**



**CONCLUSION**

The new magnesium-enhanced lime process is an improvement upon the older magnesium-enhanced lime process. The new process produces valuable by-products, gypsum, which is used to manufacture wallboard, and magnesium hydroxide. Magnesium hydroxide has been demonstrated to control emissions of sulfuric acid mist and reduce visible opacity.

Cost for installation and operation of the magnesium-enhanced lime process is competitive with the wet limestone process. Injection of by-product magnesium hydroxide into the furnace for control of sulfur trioxide and reduction in slag build-

ups can have significant cost benefit that reduces net cost of a magnesium-enhanced lime installation.

## REFERENCES

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<sup>3</sup> Source: McIlvaine Company

<sup>4</sup> M. Golightley et.al., "*Lime-Based Forced Oxidation to Gypsum at First Energy's Bruce Mansfield Station*", Proceedings: EPRI-DOE-EPA, Combined Utility Air Pollutant Control Symposium, Atlanta, GA, August 1999.

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<sup>6</sup> W. Brockman et.al., "Concept Development, Pilot Testing, and Design Leading to Conversion of the Wm. H. Zimmer FGD System to Bleed Stream Oxidation", Combined Utility Air Pollutant Control Symposium, Atlanta, GA, August 1999.

<sup>7</sup> L. Benson, M. Babu, K. Smith, "*New Magnesium-enhanced Lime FGD Process*", The Mega Symposium in conjunction with AWMA's Mercury Fate, Effects and Control Specialty Conference, August 20-23, 2001, Chicago, IL, USA

<sup>8</sup> R. Srivastava, W. Jozewicz, "*Flue Gas Desulfurization: The State of the Art*", Journal of the Air and Waste Management Association, 51: 1676-1688.

<sup>9</sup> Internal Carmeuse North America study