

**ICAC Forum '03**  
**Multi-Pollutant Emission Controls & Strategies**

**Control of Sulfur Dioxide and Sulfur Trioxide Using  
By-Product of a Magnesium-Enhanced Lime FGD System**

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**ABSTRACT**

Combustion of high-sulfur coal combined with control of nitrogen oxide emissions via selective catalytic reduction (SCR) can produce high concentrations of sulfur trioxide (SO<sub>3</sub>) in flue gas. If emitted to the atmosphere, sulfur trioxide could cause an increase in visible opacity and be a source of fine particulate.

A system has been developed for control of sulfur trioxide emissions using byproduct magnesium hydroxide from a Thiosorbic<sup>®</sup> (magnesium-enhanced lime) wet flue gas desulfurization (FGD) process. The byproduct is injected into a coal furnace at levels between the “nose” and the upper furnace, where it captures sulfur trioxide formed during combustion. 90% capture of furnace-generated SO<sub>3</sub> can be achieved. For a unit with SCR, about 70% overall capture can be achieved.

Based on successful testing in 800 MW and 1300 MW units, furnace injection of by-product magnesium hydroxide is being installed as part of an SCR installation at a Midwestern station. At this same site, for additional control of SO<sub>3</sub>, a second injection system to inject hydrated lime (calcium hydroxide) immediately after the air heaters will also be installed. The calcium hydroxide and reaction products will be collected in an electrostatic precipitator.

A magnesium hydroxide production plant can also serve as a FGD wastewater pre-treatment system. A magnesium hydroxide production system will reduce salinity and metals content of FGD wastewater. All solids produced by the magnesium hydroxide recovery process can be recycled for beneficial use.

The paper describes background on magnesium hydroxide and calcium hydroxide injection for control of SO<sub>3</sub>. Results of 800 MW and 1300 MW demonstrations of furnace injection for capture of SO<sub>3</sub> are presented. The process and equipment for production of magnesium hydroxide and its integration into a magnesium-enhanced lime FGD system are described. Expected SO<sub>3</sub> removal efficiency from using magnesium hydroxide and calcium hydroxide

injection in a >1000 MW application are discussed. Production cost of byproduct magnesium hydroxide is estimated and compared with cost of commercial magnesium hydroxide for use in SO<sub>3</sub> control.

## **INTRODUCTION**

Sulfuric acid is present in flue gases from combustion of high-sulfur coal because a small fraction of sulfur dioxide (SO<sub>2</sub>) produced, approximately 0.5 to 1.5%, is further oxidized to SO<sub>3</sub>. SO<sub>3</sub> reacts with water in flue gas to form sulfuric acid vapor. Sulfuric acid is a Toxic Release Inventory substance. Sulfuric acid can cause air heater fouling and equipment corrosion. When flue gas containing sulfuric acid vapor is rapidly cooled, as in a wet FGD system, sulfuric acid condenses to form a sub-micron aerosol mist, which scatters light and can form a visible plume.

In addition to SO<sub>3</sub> formed during combustion, selective catalytic reduction (SCR) catalysts used for NO<sub>x</sub> control further oxidize a fraction (0.5 to 1.5%) of SO<sub>2</sub> to SO<sub>3</sub>. As a result of both furnace and SCR oxidation, as much as 3% of SO<sub>2</sub> can be converted to SO<sub>3</sub>. Furthermore, on units that cycle in load, the SO<sub>3</sub> content in the furnace exit gas can limit SCR operation at lower unit load, due to the potential for forming ammonium sulfate salts that foul active catalyst sites at the lower economizer outlet flue gas temperatures.

### **Alkali Injection for SO<sub>3</sub> Control**

Injection of finely divided alkalis into flue gas has been demonstrated for removal of SO<sub>3</sub> from flue gases. Most commercial experience is from units firing high-sulfur oil where trace metals, mainly vanadium, increase oxidation of SO<sub>2</sub><sup>1</sup>. Magnesium-based compounds have been used successfully for decades for capture of SO<sub>3</sub> in oil-fired units<sup>2</sup>. Their use in coal-fired units has been limited.

Furnace injection is an attractive option for removing flue gas SO<sub>3</sub> for several reasons. Injecting alkali into the furnace maximizes residence time for alkali to react with SO<sub>3</sub> formed in the furnace, and high furnace temperatures increase diffusion rate of SO<sub>3</sub> toward alkali particles, which increases capture rate. Injection of magnesium and calcium-based alkalis into the furnace removes vapor-phase arsenic, which is a SCR catalyst poison. Finally, SO<sub>3</sub> removal upstream of the SCR system could eliminate the low load limits on SCR operation as noted earlier.

Additional benefits of removal of SO<sub>3</sub> in the furnace include reduction in deposits on heat transfer surfaces, especially the air heater. 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 further cooled without condensation of sulfuric acid. This would allow greater recovery of heat from the gas and an increase in furnace efficiency.

### ***Magnesium Hydroxide Injection***

Magnesium hydroxide [Mg(OH)<sub>2</sub>] and magnesium oxide (MgO) are the most commonly used magnesium compounds for furnace injection. After injection, Mg(OH)<sub>2</sub> loses water of hydration to become MgO at a temperature above 662°F (350°C). MgO reacts with SO<sub>3</sub> to form magnesium sulfate particles that are removed in a downstream particulate control device.

Magnesium oxide is effective because it reacts directly with SO<sub>3</sub> to form magnesium sulfate. Magnesium sulfate is water-soluble so it is unlikely to form hard-to-remove deposits on equipment and ductwork. In oil-fired units, magnesium oxide is also effective because it ties up vanadium deposits that would otherwise catalyze the oxidation of SO<sub>2</sub> to SO<sub>3</sub> in the furnace gas. In coal-fired units, it is believed that magnesium oxide can form a film on furnace heat transfer surfaces and likewise prevent catalysis of SO<sub>2</sub> to SO<sub>3</sub> by iron oxides<sup>3</sup>. Also, magnesium oxide is known to modify coal ash fusion temperatures and slag properties, so that injection of magnesium oxide can reduce furnace slagging or make slag deposits more friable.

Magnesium-based alkalis are preferred over calcium based-alkalis for furnace injection for several reasons. Magnesium does not react with SO<sub>2</sub> at furnace temperatures, so SO<sub>2</sub> does not compete with SO<sub>3</sub> for reactive sites on alkali particles. Calcium-based alkalis like hydrated lime [calcium hydroxide, Ca(OH)<sub>2</sub>] react rapidly with SO<sub>2</sub> at furnace temperature. Calcium hydroxide loses water of hydration at temperature above 1076°F (580°C) to form calcium oxide (CaO). Calcium oxide reacts with SO<sub>2</sub> to form calcium sulfate, which coats the particle surface. For removal of SO<sub>3</sub>, which would reduce the number of sites where SO<sub>3</sub> can react, a high ratio of injected calcium to SO<sub>3</sub> would be required to achieve high removal of SO<sub>3</sub> in the furnace. Also, calcium oxide and calcium sulfate particles are known to have high electrical resistivity, so injecting large amounts of calcium hydroxide into the furnace to remove SO<sub>3</sub> would lead to difficulty with ESP operation. Calcium oxide reacts with SO<sub>3</sub> to form calcium sulfate, which can form hard deposits that are only slightly soluble in water making cleaning difficult.

Although magnesium hydroxide has been shown to be effective for control of SO<sub>3</sub> and to have other benefits for furnace operation, its use in large coal-fired units has been limited by its cost. Magnesium hydroxide is generally more expensive than calcium hydroxide. Most magnesium hydroxide suitable for furnace injection is produced by precipitation with calcium hydroxide from magnesium-containing brines.

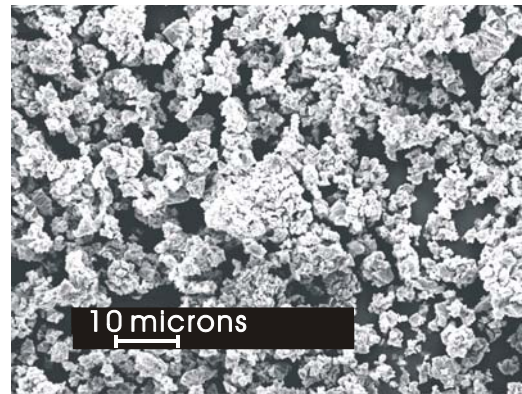
### Calcium Hydroxide Injection

Although not as effective as magnesium hydroxide for furnace injection, hydrated lime (calcium hydroxide) has good potential for control of SO<sub>3</sub> via dry injection into flue gas ahead of an ESP. The typically very short gas residence time between the air heater and ESP does not provide adequate drying time for injection of calcium hydroxide in slurry form. Also, SO<sub>2</sub> is not efficiently captured by calcium hydroxide at pre-ESP temperature of 300-350°F, whereas SO<sub>3</sub> is efficiently captured at this temperature. Table 1 shows composition of a hydrated lime that has been tested in coal-fired plants for removal of SO<sub>3</sub> via injection ahead of an ESP.

For large coal-fired plants that would use a large amount of hydrated lime annually, operating cost may be substantially reduced by installing equipment for on-site production of hydrated lime from quicklime (calcium oxide). This may be especially true for plants with lime-based wet FGD systems that already include lime unloading and storage facilities. In this situation a conventional dry lime hydrator would impose a relatively small footprint and a 5-TPH (Ca(OH)<sub>2</sub> basis) unit would have an installed cost less than \$2-million.

**Table 1.** Analysis and SEM Image of Hydrated Lime (Calcium Hydroxide)

Hydrated Lime Chemical Analysis	
Ca(OH) <sub>2</sub> , wt. %	92
CaO, wt. %	70.7
MgO, wt. %	3.0
Inerts, wt. %	2.4
BET Specific Surface Area, m <sup>2</sup> /g	16
LOI at 600°C	18.6
Particle Size, mean	12 micron



A critical characteristic of hydrated lime listed in Table 1 is BET specific surface area. The BET specific surface area indicated above is the result of traditional dry hydration where slaking temperature ranges between 195 to 212 degrees F, corresponding to about 0.5% free moisture content of the hydrated lime product. Reactivity of hydrated lime has been shown to be directly related to BET specific surface area implying that more efficient use of hydrated lime results compared to traditionally produced hydrated lime. Lhoist claims SO<sub>3</sub> removal of at least 95% using their high specific surface area hydrated lime product at a Ca(OH)<sub>2</sub>/(HF+SO<sub>3</sub>) ratio close to 1.0 as compared to conventional hydrated lime ratio between 1.4 and 1.7<sup>4</sup>.

Other methods of maximizing BET surface area when producing hydrate have been discussed extensively in literature. A common thread in this literature is a direct relationship between either the use of water in significant excess of the stoichiometric requirement or the lower slaking temperature that results by the use of excess water and the resulting BET specific surface area.

A Swedish study at the Lund Institute of Technology indicates, regardless of lime type or quality, a direct relationship between the amount of water used in dry slaking and the resulting BET specific surface area of the hydrated lime. The study also suggests that specific surface area may be influenced by the lowering of slaking temperature through the addition of extra water. Lime from Sweden and Poland was dry slaked at varying mass water to mass lime ratio of between ~0.45 (31% moisture) to 0.7 (41% moisture) that resulted in an improvement of BET specific surface area from ~10 up to 30 m<sup>2</sup>/g. The study does not provide dry slaking temperature data<sup>5</sup>.

The obvious problems using extra water in dry slaking include the expense of transporting water and possible problems handling material containing more moisture than typical. Recognizing both the promise and problems associated with dry slaking with excess water, both Alstom Power and Graf/Wulff promote on site dry hydration of lime in their respective dry FGD processes.

Alstom's Flash Dryer Absorber dry FGD process employs an integrated lime hydrator that dry slakes lime at cooler temperatures to produce hydrated lime with BET surface area greater than 30 m<sup>2</sup>/g. Alstom adds another benefit to on-site hydration in that reagent and transportation cost of lime per unit mass is less expensive than that of hydrated lime due to lime's higher bulk density<sup>6</sup>.

Wulff has developed a fluid bed lime hydrator where water is injected at a rate of 50% in excess of the stoichiometric amount needed hydration of lime (~10% moisture)<sup>7</sup>. Although no specific BET specific surface area data is mentioned by Wulff, the hydrated lime produced in the fluid bed hydrator is described as "highly reactive", implying an enhancement of the specific surface area.

## **PRODUCTION OF MAGNESIUM HYDROXIDE FROM THE MAGNESIUM-ENHANCED LIME FGD PROCESS**

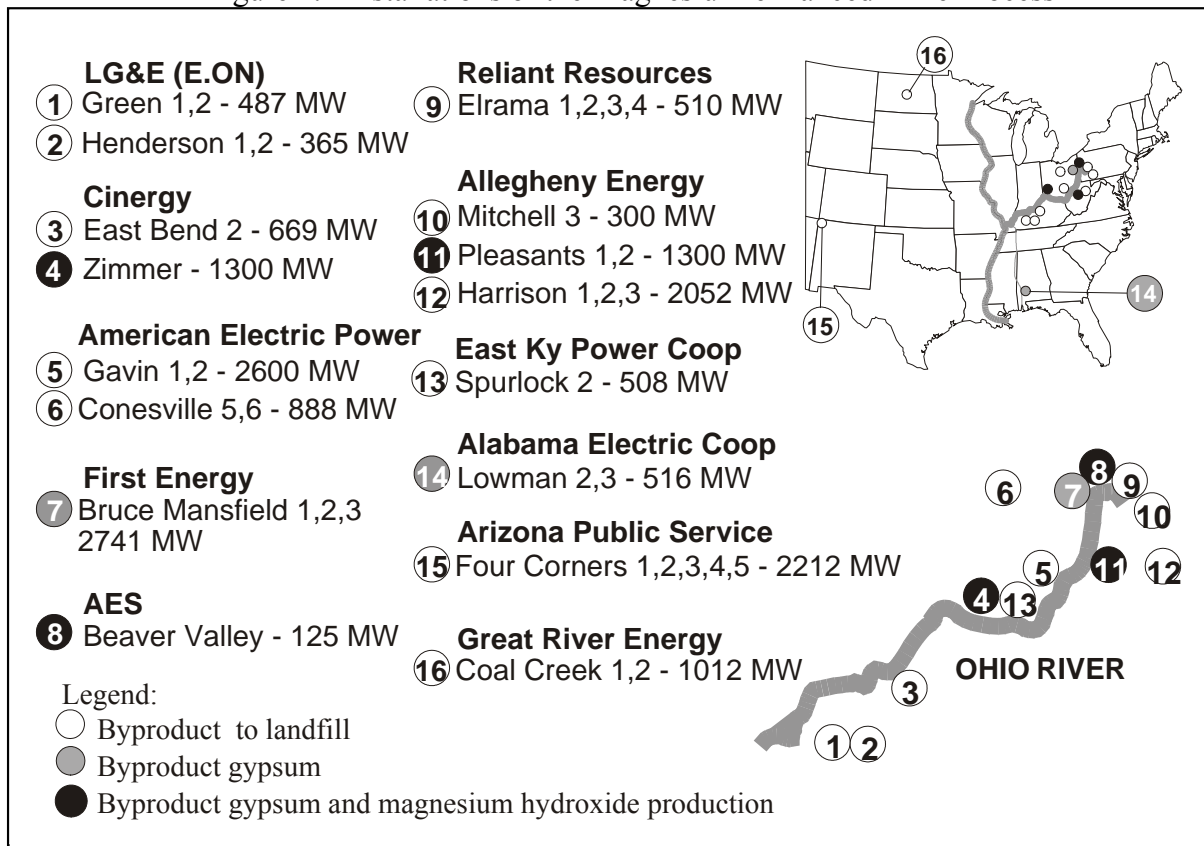
Magnesium hydroxide that is a byproduct of a magnesium-enhanced (Thiosorbic<sup>®</sup>) lime wet flue gas desulfurization (FGD) process has been demonstrated to be suitable and equally effective as commercially-available magnesium hydroxide for furnace injection for removal of SO<sub>3</sub>. The byproduct can be produced and used on-site, which avoids transportation cost.

The process for production of by-product magnesium hydroxide was invented by Carmeuse Lime and developed in a pilot project in 1995 at an Ohio based utility. A midwestern utility, the Ohio Coal Development Office, the Electric Power Research Institute, and Carmeuse Lime sponsored the project.

The Thiosorbic FGD process is used in about 17700 MW of coal-fired electric generating capacity in the United States. Figure 1 shows power generating stations that use the process. Two stations totaling about 1500 MW currently produce magnesium hydroxide. A third midwestern station is currently installing equipment to product magnesium hydroxide, as discussed later.

An additional benefit of magnesium hydroxide recovery is where FGD wastewater treatment is required. The wastewater contains magnesium, chloride, and sulfate ions and small amounts of heavy metals removed from the flue gas. Treatment of this liquid with lime in the magnesium hydroxide recovery equipment precipitates magnesium and sulfate ions, which reduces dissolve solids, and precipitates metals along with the magnesium hydroxide. When the recovery magnesium hydroxide is injected into the furnace for control of SO<sub>3</sub> emissions, the heavy metals may be removed with flyash in particulate removal equipment.

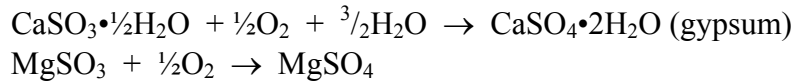
Figure 1. Installations of the Magnesium-enhanced Lime Process



The magnesium-enhanced FGD process uses lime that contains 2-8 weight percent magnesium oxide (MgO) and 83-91 percent calcium oxide. MgO in the lime reacts with SO<sub>2</sub> to form soluble magnesium sulfite (MgSO<sub>3</sub>), which accumulates in absorber slurry. Magnesium sulfite acts as a pH buffer that greatly increases SO<sub>2</sub> mass transfer compared with systems where a pH buffer is absent. As a result, greater than 95 percent SO<sub>2</sub> removal is achieved with low absorber liquid-to-gas ratios. For example, one system achieved 96% SO<sub>2</sub> removal in performance tests with L/G of 21-GPM per 1000-ACFM (3 liters per cubic meter.)<sup>8</sup> Magnesium sulfite also prevents calcium-based deposits from forming on the insides of the absorber. Magnesium-enhanced lime process chemistry and characteristics are discussed in detail elsewhere<sup>9</sup>.

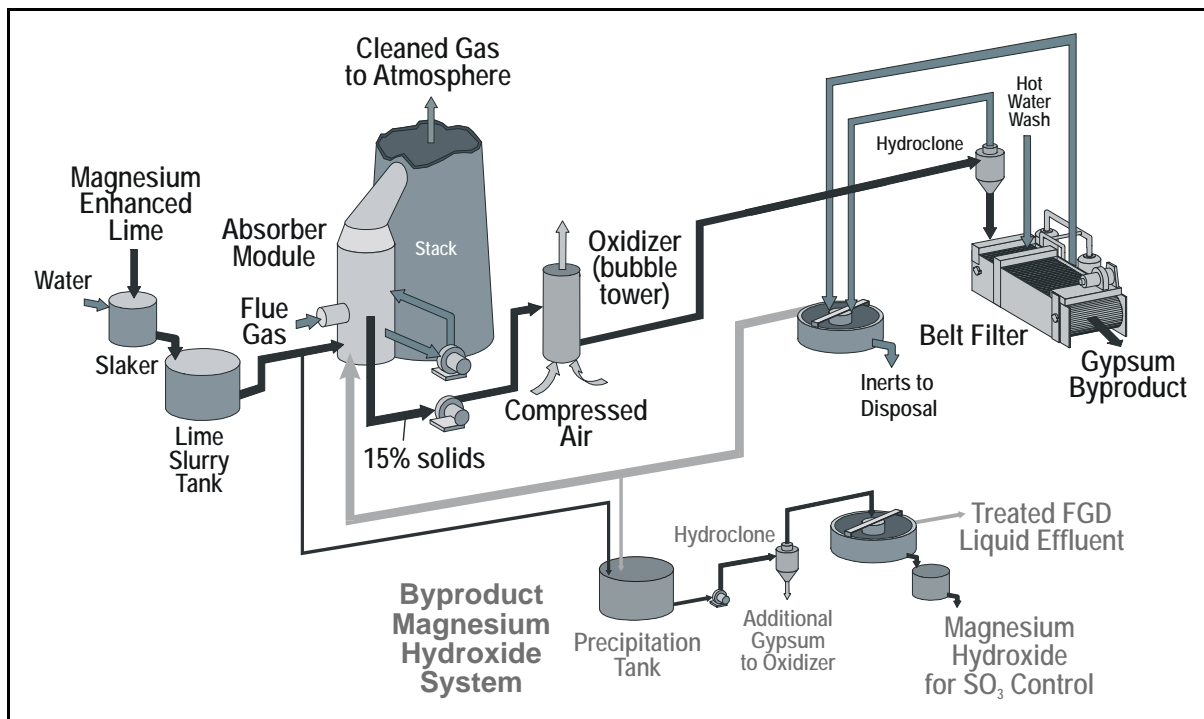
In the magnesium-enhanced lime process, magnesium salts accumulate in FGD process liquid to a magnesium ion concentration of about 5000-15000 mg/liter. This high concentration of magnesium ions provides the source for production of byproduct magnesium hydroxide.

Figure 2 shows a flow diagram of the magnesium-enhanced lime FGD 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:



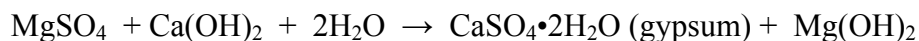
Gypsum is recovered by filtration and is sold to either a wallboard or a cement manufacture. Most of the filtrate is returned to the absorber, while a portion of the filtrate is withdrawn as FGD wastewater to purge accumulated salts. The wastewater, containing  $\text{MgSO}_4$  and  $\text{MgCl}_2$ , is available for production of magnesium hydroxide.

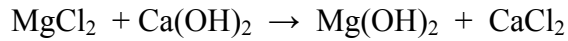
Figure 2. Magnesium-enhanced Lime Process with Magnesium Hydroxide Recovery



### System for Production of By-Product Magnesium Hydroxide

Magnesium hydroxide is produced by adding slaked lime (calcium hydroxide with a small amount of magnesium hydroxide) to the wastewater that is withdrawn from the FGD system.  $\text{MgSO}_4$  undergoes a double-decomposition reaction with calcium hydroxide to precipitate both magnesium hydroxide and gypsum. Magnesium chloride also reacts with calcium hydroxide to precipitate additional magnesium hydroxide:





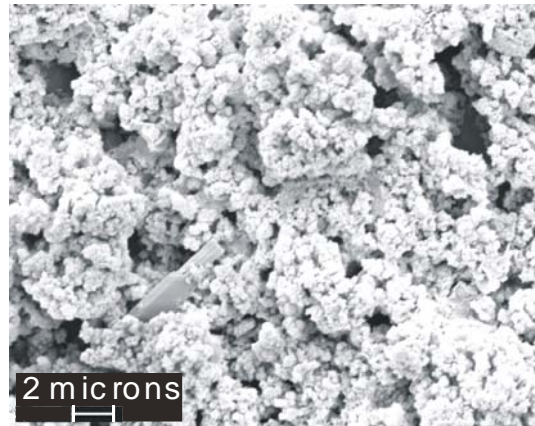
Magnesium hydroxide particles formed are very small, 3 microns average, while the gypsum particles are much larger, 60 microns average.

The bottom of Figure 2 shows equipment used for magnesium hydroxide recovery. The equipment is similar to that used in wastewater treatment. It includes a precipitation tank where slaked lime is added to FGD wastewater; pH is controlled to between 9.5 and 10. At this pH essentially all magnesium precipitates as magnesium hydroxide. Most of the sulfate ions precipitate as gypsum. Liquid containing magnesium hydroxide and gypsum flows from the precipitation tank to hydroclones for separation of magnesium hydroxide and gypsum particles; their large size difference allows efficient separation. Separated gypsum is returned to the oxidizer, where it becomes part of the main gypsum stream and increases gypsum production. Separated magnesium hydroxide flows to a gravity thickening tank, where it settles to a slurry containing 20% solids. This slurry is available for furnace injection.

Table 2 provides typical properties of recovered by-product  $\text{Mg}(\text{OH})_2$ . The magnesium hydroxide has a high specific surface area, about 55 square meters per gram.

**Table 2.** Analysis and SEM Image of By-Product Magnesium Hydroxide

Magnesium Hydroxide Chemical Analysis	
Mg(OH) <sub>2</sub> , wt. %	75
Gypsum as CaSO <sub>4</sub> •2H <sub>2</sub> O, wt. %	19
Inerts, wt. %	6
Total Suspended Solids in Slurry, %	20
BET Specific Surface Area, m <sup>2</sup> /g	55
Particle Size D50	3 micron



From the stoichiometry of the precipitation reactions above, about one ton of lime is required for each ton of magnesium hydroxide produced. Since lime used in large wet FGD systems is low in cost (about \$50 per ton) compared with commercially-produced magnesium hydroxide (about \$200 per ton), and since the byproduct can be used on-site with no transportation charge, the production cost of byproduct magnesium hydroxide is low. For a magnesium-enhanced lime FGD system using lime with 6 weight percent MgO, and assuming 100% recovery, lime use increases by about 9%.

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

In 2000 and 2001, the U.S. Department of Energy's National Energy Technology Laboratory (DOE/NETL) tested full-scale furnace injection of by-product magnesium hydroxide at First Energy's 800 MW Bruce Mansfield Unit 3 and American Electric Power's 1300 MW Gavin Unit 1 to determine efficiency with which it could control sulfur trioxide emissions. Co-funders included EPRI, First Energy, AEP, TVA, and Carmeuse Lime. A detailed description of the testing and results is described elsewhere<sup>10, 11</sup>. The results are summarized in the following sections.

### **800 MW Demonstration**

The 800 MW unit typically burns a bituminous 4-4.5% sulfur coal. The boiler is equipped with two air heaters following the economizer section. The average flue gas temperature at the outlet of the air heaters is controlled to about 320°F (160°C) to avoid sulfuric acid condensation on air heater heat transfer surfaces. Flue gas from each of the two air heaters splits into two duct runs, each of which goes to an ESP followed by an induced draft (ID) fan. Downstream of the ID fans, the flue gas flows to a common plenum, and then the gas flow splits to up to five horizontal-gas-flows, FGD system absorber modules (four normally operate at full load). The scrubbers use a magnesium-enhanced, Thiosorbic<sup>®</sup> lime slurry reagent. The flue gas in the stack is saturated at a temperature of about 130°F (54°C).

Testing was conducted in two parts. The first were short-term tests of one to two weeks for the purpose of screening various alkalis to determine the best for longer-term testing. Three different magnesium-based alkali slurries were tested, including pressure-hydrated dolomitic lime, commercial magnesium hydroxide, and byproduct magnesium hydroxide. In these screening tests, slurries were injected through up to six air-atomizing nozzles inserted into only one-half of the front wall of the boiler and ahead of one of the two air heaters and two of the four ESP's. Two injection locations were used during the tests. The first was across from the "nose"; the second was near the pendant super heater platens.

Overall, the results showed that highest SO<sub>3</sub> removal was obtained with byproduct magnesium hydroxide or commercial magnesium hydroxide and with the injection location near the super heater. With byproduct magnesium hydroxide, over 90% SO<sub>3</sub> removal (based on ESP outlet concentration) was obtained at a Mg:SO<sub>3</sub> ratio of about 7:1. SO<sub>3</sub> concentration at the ESP inlet was reduced to 3-4 ppm, while ESP outlet concentration was 2 ppm. At these very low SO<sub>3</sub> concentrations, a brief increase in opacity monitor reading was observed which was due solely to the great reduction in SO<sub>3</sub> concentration and its effect on ash conditioning. The unit has relatively small ESP's with specific collection area (SCA) of 100 ft<sup>2</sup>/1000-ACFM. Opacity returned to normal when magnesium hydroxide feed rate was reduced to allow ESP inlet SO<sub>3</sub> concentration to increase to about 9 ppm.

In the long-term test, magnesium hydroxide was injected to treat 100% of the flue gas. Slurry was injected through ten air-atomizing nozzles through the front boiler wall near the pendant super heater. Injection was continued 24 hours per day for 24 days.

Figure 3. Furnace SO<sub>3</sub> Removal vs. Mg:SO<sub>3</sub> Reagent Ratio for 800 MW Test

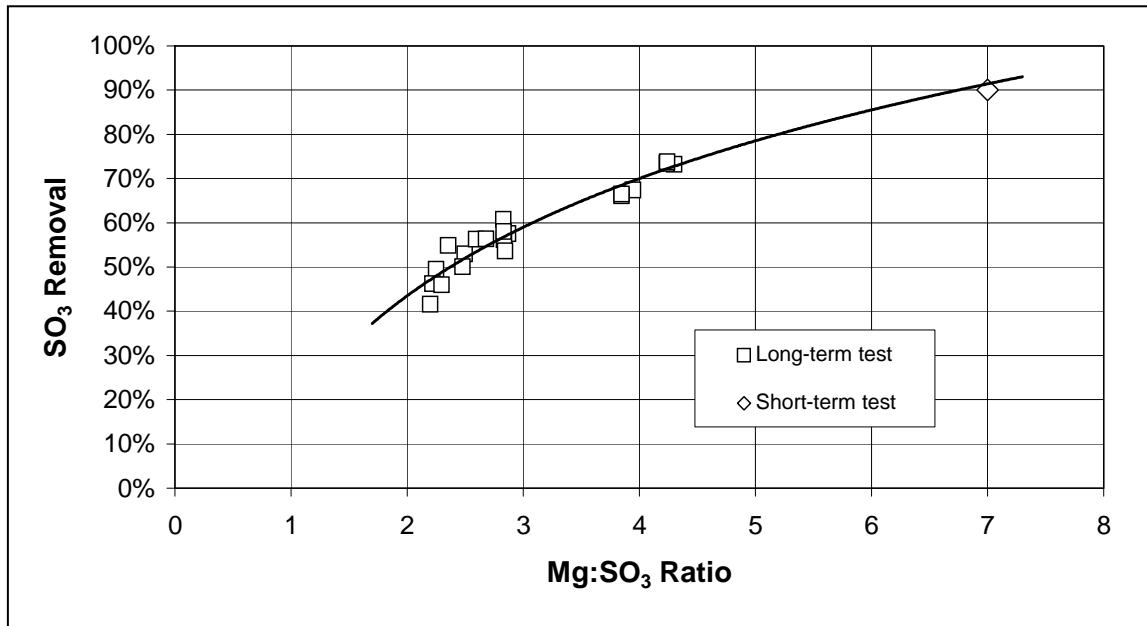


Figure 3 shows SO<sub>3</sub> removal efficiency vs. Mg:SO<sub>3</sub> ratio for the 800 MW tests. SO<sub>3</sub> removal efficiency was determined by comparing the results with baseline ESP outlet SO<sub>3</sub> concentration. Baseline SO<sub>3</sub> concentration was 32 to 39 ppmv (adjusted to 3% O<sub>2</sub>). The results show that 90% SO<sub>3</sub> removal was obtained at a Mg:SO<sub>3</sub> ratio of about 7. The plot includes a result from the short-term test. Good agreement is seen between the short-term result and a logarithmic extrapolation of data from the long-term test.

In addition to a large reduction in SO<sub>3</sub> concentration, stack gas visual opacity was greatly reduced during magnesium hydroxide injection compared with baseline conditions.

SCR catalyst test coupons inserted in the gas stream after the economizer prior to the magnesium hydroxide injection tests showed no reduction in activity or pore volume compared with coupons insert during the baseline period. Also, accumulation of arsenic, a SCR catalyst poison, on the catalyst surface was reduced by 94% following 500 hours of operation with magnesium hydroxide compared with a similar period of operation under baseline conditions.

No adverse accumulation of slag was observed during the test period.

### 1300 MW Demonstration

A second full-scale demonstration of magnesium hydroxide injection was conducted on a 1300 MW unit. The unit typically burns bituminous coal with 3.5-4% sulfur. Flue gas from the economizer splits into three gas paths. Each path flows to an SCR reactor. About 1% of SO<sub>2</sub> in the flue gas is further oxidized to SO<sub>3</sub> in the SCR. Flue gas then flows to three air heaters. Flue gas leaving the air heaters is normally maintained at about 350-360 °F to avoid sulfuric acid

condensation in the air heaters. The gas then flows to ESP's, then to a Thiosorbic lime FGD system.

Tests on the 1300 MW unit differed from those on the 800 MW unit due to the presence of an SCR. In this 16 day test injection was continued round the clock. Two injection locations in the furnace were tested. In one mode, slurry was injected via air-atomizing nozzles inserted in 10 inspection ports on the forward wall across from the pendant super heater tubes to treat 100% of the gas. The second mode was to inject 60% of the slurry at this location and 40% through nozzles located across from the "nose." Better removal of furnace-generated SO<sub>3</sub> was obtained in this later mode.

Figure 4 shows SO<sub>3</sub> removal efficiency versus Mg:SO<sub>3</sub> ratio for furnace-generated SO<sub>3</sub> for the byproduct magnesium hydroxide tests. SO<sub>3</sub> removal efficiency was determined by comparing the results with baseline economizer outlet SO<sub>3</sub> concentration. Baseline economizer outlet SO<sub>3</sub> concentration was 37 ppmv. The results show that 90% of furnace-generated SO<sub>3</sub> was removed at a Mg:SO<sub>3</sub> ratio of about 7. This is in very good agreement with results from the 800 MW demonstration. (At lower Mg:SO<sub>3</sub> ratios, SO<sub>3</sub> removal is slightly lower than in the 800 MW tests because the 800 MW results in Figure 3 are for measurements at the ESP outlet. A small percentage of the total removal occurs across the ESP.)

Figure 4. Furnace SO<sub>3</sub> Removal vs. Mg:SO<sub>3</sub> Reagent Ratio for 1300 MW Test

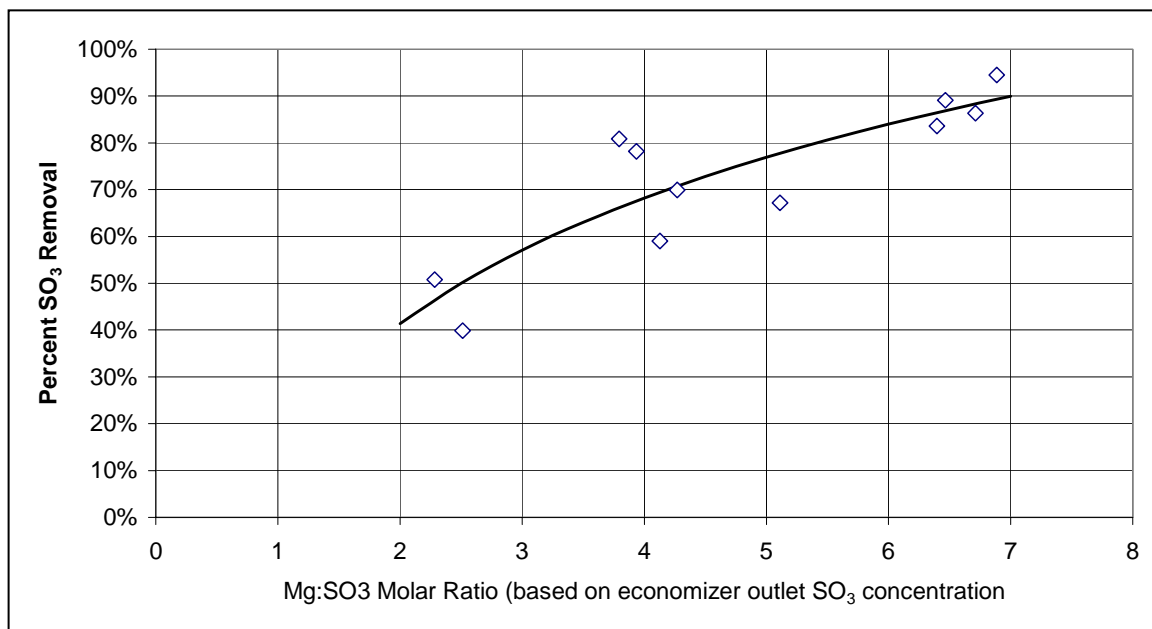
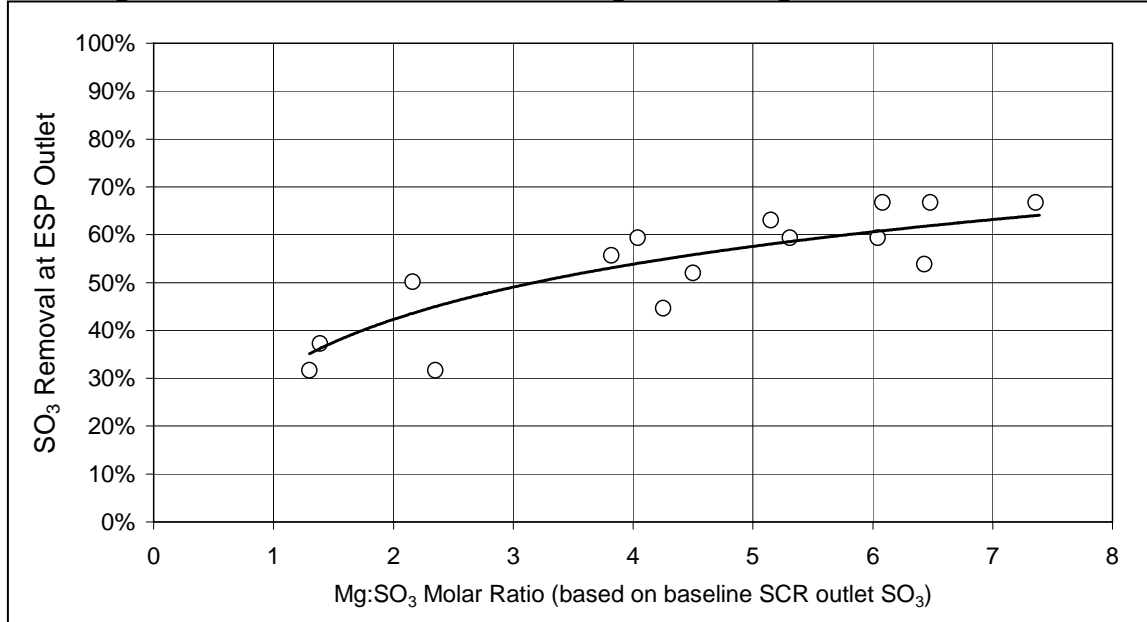


Figure 5 shows SO<sub>3</sub> removal efficiency versus Mg:SO<sub>3</sub> ratio including both furnace-generated and SCR-generated SO<sub>3</sub>. For overall removal, little difference between furnace injection locations was observed, so the figure includes results for injection at both locations discussed above. The results show that at a Mg:SO<sub>3</sub> ratio (based on baseline SCR outlet SO<sub>3</sub> concentration of 65 ppm) of about 5, 60% overall SO<sub>3</sub> removal was achieved. At a Mg:SO<sub>3</sub> of 7, 67% overall SO<sub>3</sub> removal was obtained.

Figure 5. Overall SO<sub>3</sub> Removal including SCR vs. Mg:SO<sub>3</sub> Ratio for 1300 MW Test



Magnesium hydroxide injection caused a significant reduction in opacity monitor readings.

Stack visual opacity was significantly reduced during magnesium hydroxide injection.

As occurred during the 800 MW demonstration tests, byproduct magnesium hydroxide injection caused some drop in secondary current in the first two fields of the ESP. The remaining four fields were unaffected. However, neither ESP outlet opacity nor particulate loading indicated increased particulate loading.

Opacity monitor readings actually fell significantly during magnesium hydroxide injection, due mainly to reduction in SO<sub>3</sub> concentration at the ESP outlet. Baseline opacity ranged from 16 to 20%. During magnesium hydroxide injection at greater than a Mg:SO<sub>3</sub> ratio of 3, opacity readings ranged from 10 to 15% at full load. Measurements of sulfuric acid mist during baseline and during sorbent injection confirmed that the opacity decrease was due to elimination of acid mist during sorbent injection.

No adverse impact on boiler slagging was observed during sorbent injection. Analysis of slag samples indicated that MgO was not appreciably incorporated into the slag, which is necessary to alter slag properties. For injection in the super heater region, flue gas temperature was probably already below the ash fusion temperature, so MgO was unlikely to become incorporated into the slag.

Commercial magnesium hydroxide was also tested. Overall, the results showed about the same SO<sub>3</sub> removal performance for both commercial and byproduct magnesium hydroxide.

The results of the 800 and 1300 MW demonstration tests served as a basis for a new permanent commercial installation of an SO<sub>3</sub> control system using byproduct magnesium hydroxide injection, described in the following section.

## **COMMERCIAL APPLICATION OF MAGNESIUM HYDROXIDE INJECTION FOR SO<sub>3</sub> REMOVAL**

Coal fired units that burn bituminous coal with about 3.5-4% sulfur coal, typically experience about 1% oxidation of SO<sub>2</sub> to SO<sub>3</sub> occurring in the furnace. SCR reactors used to treat flue gas for NO<sub>x</sub> can be expected to contribute an additional 1% oxidation of SO<sub>2</sub> to SO<sub>3</sub>. Anticipating this outcome, a midwestern utility with existing magnesium-enhanced lime FGD is installing an SO<sub>3</sub> mitigation system as part of the SCR installation. The SO<sub>3</sub> mitigation system includes a byproduct recovery process that will recover magnesium hydroxide from an FGD liquid purge stream.

To achieve 90% overall removal of SO<sub>3</sub>, including both furnace-generated and SCR-generated SO<sub>3</sub>, the system will include a two-stage alkali injection system. In the first stage, byproduct magnesium hydroxide slurry will be injected into the furnace through air-atomizing nozzles located in the front wall of the furnace. In the second stage, hydrated lime [calcium hydroxide, Ca(OH)<sub>2</sub>] will be injected as a dry powder into flue gas immediately after the air heaters. Hydrated lime injection along with SO<sub>3</sub> removal across FGD absorbers is expected to capture 90% of SO<sub>3</sub> not captured by magnesium hydroxide.

The magnesium hydroxide system includes equipment for injection of slurry into the furnace through air-atomizing nozzles located at levels between the nose and the super heater platens. Byproduct magnesium hydroxide will contain about 20% suspended solids of which at least 65% is Mg(OH)<sub>2</sub>.

The design maximum magnesium hydroxide injection rate is approximately 3 tons/hr of Mg(OH)<sub>2</sub> to achieve 90% removal of furnace-generated SO<sub>3</sub>. The capacity of the byproduct magnesium hydroxide production plant will be sufficient to supply nearly this entire requirement. Commercial magnesium hydroxide will be used as a backup supply. Assuming 1% conversion of SO<sub>2</sub> to SO<sub>3</sub> in the furnace, the injection rate is equivalent to a design molar Mg:SO<sub>3</sub> molar ratio of 8. This value compares with the Mg:SO<sub>3</sub> ratio of about 7 that was required to achieve 90% removal of furnace-generated SO<sub>3</sub> in the 800 MW and 1300 MW demonstration tests. The injection rate required will depend on coal chemistry, boiler conditions, percent removal requirements and Mg(OH)<sub>2</sub> reactivity. Optimizing furnace injection locations may further reduce this molar ratio.

Injection of hydrated lime ahead of an ESP has been tested at 1300 MW for post-SCR SO<sub>3</sub> mitigation via injection immediately after the air preheater<sup>12</sup>. The design maximum injection rate of hydrated lime is approximately 4 tons/hr to achieve 90% removal of SCR-generated SO<sub>3</sub>. Assuming 1% conversion of SO<sub>2</sub> to SO<sub>3</sub> in the SCR, and 4.1% sulfur in coal, this injection rate is equivalent to a design maximum molar Ca(OH)<sub>2</sub> to SCR-generated-SO<sub>3</sub> ratio of 7.7.

## **FGD Purge Stream Pre-Treatment**

A byproduct magnesium hydroxide production plant can also serve as a pre-treatment system for the FGD liquid purge stream. Precipitation of magnesium hydroxide and gypsum can reduce dissolved solids content by 80% with over 97% of magnesium ions and over 90% of sulfate ions removed from the water. In addition, metals that are soluble at the acidic pH (5-6) in FGD liquid can be removed by precipitation with slaked lime with the magnesium hydroxide recovery plant operating at pH of 9.5-10.

The list of equipment needed for the byproduct recovery plant includes an agitated tank where lime slurry and FGD liquor are mixed resulting in the precipitation of gypsum and magnesium hydroxide. The resulting slurry is pumped to a bank of hydroclones where the distinctly different gypsum and magnesium hydroxide crystals are separated. The resulting gypsum slurry is directed to the existing FGD oxidizer and can become part of any current FGD gypsum production. Magnesium hydroxide slurry is directed to a thickener from which magnesium hydroxide slurry will be pumped to a storage tank and subsequent use. Treated FGD liquor from the clarifier overflow will be discharged to an onsite pond system where it will be mixed with all other station water discharges.

## **SO<sub>3</sub> CONTROL COSTS**

Byproduct magnesium hydroxide and calcium hydroxide can be significantly less expensive than other reagents for SO<sub>3</sub> control. Byproduct magnesium hydroxide is produced and used on site, which eliminates transportation cost. Equipment for recovery of magnesium hydroxide is relatively small, consisting mainly of a lime reactor and thickener as in a wastewater treatment plant. For FGD systems that require wastewater treatment, the magnesium hydroxide recovery system might replace the first stage of typical wastewater treatment and greatly reduce the volume of wastewater treatment sludge.

## **Byproduct Magnesium Hydroxide Production Cost**

A study was conducted by the Carmeuse North America Technology Center to estimate production cost of byproduct magnesium hydroxide for a >1000 MW unit equipped with a Thiosorbic lime wet FGD system. Installed cost for a system to produce about 3 tons per hour of Mg(OH)<sub>2</sub> was estimated to be \$5.4 million, or \$4/kW. Assuming an annual operating load factor of 75% and production of 19,853 tons per year of Mg(OH)<sub>2</sub> for SO<sub>3</sub> control, operating cost (excluding capital cost) to produce the byproduct was found to be \$67 per ton of Mg(OH)<sub>2</sub>. This cost includes cost of lime, about \$50 per ton, required for Mg(OH)<sub>2</sub> production.

## **Comparison of SO<sub>3</sub> Control Reagent Costs**

Annual cost savings from using byproduct magnesium hydroxide for SO<sub>3</sub> control compared with using commercial magnesium hydroxide would be substantial. Based on annual Mg(OH)<sub>2</sub> use of 19,853 tons per year, byproduct production cost of \$67 per ton, and cost for

commercial magnesium hydroxide of \$210 per ton, annual savings would be about \$2.5 million. Based on the study above, payback period for the magnesium hydroxide production equipment would be 2 years.

## **CONCLUSION**

A system has been developed for control of sulfur trioxide emissions using byproduct magnesium hydroxide from a Thiosorbic<sup>®</sup> (magnesium-enhanced) lime wet flue gas desulfurization (FGD) process. The byproduct is injected into a coal furnace where it captures sulfur trioxide formed during combustion. 90% capture of furnace-generated SO<sub>3</sub> can be achieved. For a unit with SCR, about 70% overall capture can be achieved.

For additional control of SO<sub>3</sub>, a second injection system can be used to inject dry hydrated lime (calcium hydroxide) immediately after the air heaters. Commercial lime hydrators are available that produce hydrated lime having significantly greater BET surface area and therefore more reactivity resulting in more efficient use.

Based on successful testing in 800 MW and 1300 MW units, a system for production and use of byproduct magnesium hydroxide for SO<sub>3</sub> control is being installed at a large midwestern station as part of an SCR installation. The magnesium hydroxide production plant will also serve as a FGD wastewater pre-treatment system.

Production cost of byproduct magnesium hydroxide is low, about \$67 per ton, compared with commercial magnesium hydroxide, about \$200 per ton, which allows a rapid return on investment in equipment for byproduct production.

## **DISCLAIMER**

Neither Carmeuse North America makes any warranty or representation, expressed or implied, and assumes no liability with respect to the use of, or damages resulting from the use of any information, apparatus, method or process disclosed in this document.

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## KEY WORDS

Sulfur trioxide capture; SO<sub>3</sub>; magnesium-enhanced lime; Thiosorbic lime; FGD byproducts; sulfur trioxide control costs.