

NEW MAGNESIUM – ENHANCED LIME FGD PROCESS

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ABSTRACT

Dravo Lime Inc. has developed a new magnesium-enhanced lime (MEL) based wet FGD process. This process is an improvement upon the older magnesium-enhanced lime based FGD process, which has been in use for the past 25 years and serves 15,700 MW of generating capacity. In the year 2000, 4,300 MW of the older magnesium-enhanced lime FGD capacity was converted to improved versions that produce gypsum rather than calcium sulfite.

This paper describes the new process, installations using this process and discusses performance data. This new process can obtain the high SO₂ removal efficiency of 99% which is the major hallmark of the older process while scrubbing flue gas with high inlet SO₂. In addition, this process can produce gypsum of 99% purity and obtain a reagent utilization of 99.9%. The new process can also produce byproduct Mg(OH)₂ (magnesium hydroxide) if desired.

INTRODUCTION

The conventional natural oxidation MEL (Thiosorbic[®]) FGD process has been in commercial use in the US since the early 1970's and has served the needs of the coal fired utility industry extremely well and continues to do so now. It served a base of 15,700 MW of generation capacity till recently. One significance of the MEL FGD has always been its capability for very high SO₂ removals due primarily to the highly alkaline scrubbing liquor resulting from the presence of soluble magnesium sulfite. This high alkalinity allows use of small scrubbers with a low liquid-to-gas ratio (L/G). Since the scrubber liquor typically contains less than 100 ppm of dissolved calcium ions and thus precludes potential for gypsum scaling when the soluble magnesium concentration is maintained at the desired level, the system also has a high availability. The byproduct of this well known process is principally calcium sulfite solids with some natural oxidation (10-20% mole percent) present. Table 1 shows the list of utilities currently using the MEL FGD. Those units utilizing the new process to produce gypsum are noted with an asterisk.

Table 1. List of Utilities with MEL FGD

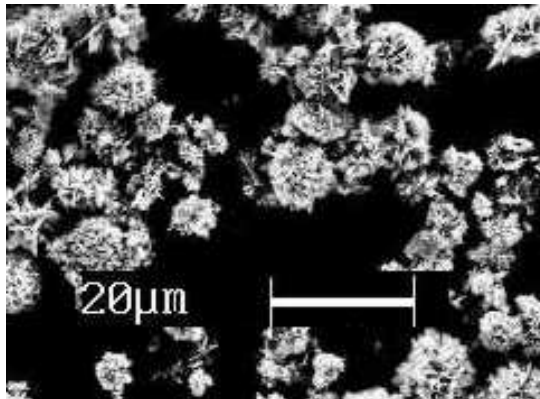
COMPANY	UNIT	MW
Alabama Electric Cooperative	Lowman 2 *	258
	Lowman 3 *	258
Allegheny Energy Supply	Harrison 1	680
	Harrison 2	680
	Harrison 3	680
	Mitchell 3	300
	Pleasants 1 *	684
	Pleasants 2 *	684
American Electric Power	Conesville 5	444
	Conesville 6	444
	Gavin 1	1,397
	Gavin 3	1,397
Applied Energy Services	Beaver Valley *	140
Arizona Public Service	Four Corners 1	170
	Four Corners 2	170
	Four Corners 3	220
WKE	Green 1	231
	Green 2	223
	Henderson 1	175
	Henderson 2	175
CINergy	East Bend 2	640
	Zimmer 1 *	1,397
Orion Power	Elrama 1	80
	Elrama 2	80
	Elrama 3	100
	Elrama 4	165
First Energy	Mansfield 1	917
	Mansfield 2	917
	Mansfield 3 *	917
* These units have the new MEL oxidized process		

In the year 2000 four of the major utility plants converted to improved versions of the MEL oxidized FGD process. Some of these larger plants and other smaller conversions were covered in detail in earlier presentations.^{1,2,3} Three of the four larger plants produces gypsum to supply feed material to new modern high-speed wallboard plants. Prior to this conversion the plants were land-filling the FGD solids via a fixated land based disposal method following primary (and in one case a secondary) dewatering followed by mixing with fly ash and stabilizing with lime. It is well known in this industry that dewatering primarily sulfite solids from the unoxidized MEL FGD system produces at best a filter cake of 40-50% solids which needs a large amount of fly ash (usually all that is available in the plant) to fixate the wet material. The new process

enables the utility customer to consider alternate uses for the fly ash since it is not needed for stabilization.

Figure 1 depicts the highly porous crystalline structure of the typical MEL FGD byproduct calcium sulfite.

Figure 1. SEM Image and Analysis for Typical Calcium Sulfite Feed Material



ANALYSIS	TYPICAL VALUES
Filter Cake	
Solids, wt %	40-45
CaO, wt %	30-35
MgO, wt %	3.0-4.0
Particle Size D50	6-10 micron

The incentives for the utilities to consider switching to the new oxidized MEL process relate to, among others, a perceived window of demand for synthetic gypsum for the new efficient wallboard plants and avoidance of investment to prepare more landfill area needed for extended periods into the future. The environmentally aesthetic desire to produce a usable product from an otherwise waste is also a significant factor. The new wallboard plants are capable of using 100% synthetic gypsum thus minimizing the need for dependence on mined natural rock.

The recently converted major oxidized MEL operations are:

- Unit #3 of First Energy’s Mansfield station in Shippingport, PA. (917 MW). The gypsum is supplied to a new National Gypsum wallboard plant.
- Pleasants Units 1 and 2 of Allegheny Energy on Willow Island, WVA. (2 x 684 MW). The gypsum is supplied to a new US Gypsum wallboard plant.
- Zimmer station of CENergy, Moscow, OH. (1,397 MW). The gypsum is supplied to a new Lafarge Gypsum wallboard plant.
- Lowman Station Units 2 and 3 of Alabama Electric, Leroy, AL. (2 x 258 MW). The gypsum is sold to a cement producer and agricultural interests.

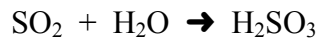
Two of the converted stations listed in Table 1 also make a byproduct magnesium hydroxide [Mg(OH)₂]. The byproduct Mg(OH)₂ is a desirable acid neutralization reagent and can be used in the utility plant for a number of beneficial purposes.

BLEED STREAM OXIDATION (BSO)

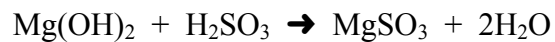
Process Chemistry

Dravo's conventional Thiosorbic[®] FGD process takes advantage of the relative high solubility of magnesium to increase the alkalinity of the scrubbing liquor. Magnesium enhanced quicklime contains 3-7% MgO and 90-95% CaO that when slaked, produces a reagent slurry comprised of magnesium hydroxide, Mg(OH)₂, and calcium hydroxide, Ca(OH)₂, that is added to the recycle tank for pH control of the scrubbing liquor.

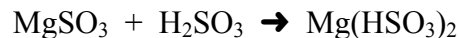
When SO₂ from the flue gas is absorbed in an aqueous solution it forms sulfurous acid, H₂SO₃.



The capacity for SO₂ absorption is limited unless an alkaline species is available to react with the sulfurous acid present. The magnesium hydroxide [Mg(OH)₂] from the lime slurry reacts with dissolved sulfur dioxide (as H₂SO₃) in either the recycle tank or absorber to form the soluble alkaline salt, magnesium sulfite (MgSO₃).



This species rapidly neutralizes additional absorbed SO₂ forming magnesium bisulfite [Mg(HSO₃)₂], providing additional SO₂ scrubbing capacity as compared to systems where magnesium sulfite is not present.



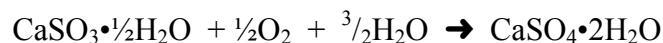
Sulfites reacting with Ca(OH)₂ produces calcium sulfite hemihydrate [(CaSO₃•1/2H₂O)] that immediately precipitates in the recycle tank. One mole of calcium hydroxide [Ca(OH)₂] from the blend of magnesium hydroxide and lime slurries reacts with one mole of Mg(HSO₃)₂ to form one mole of calcium sulfite solids [CaSO₃(s)] and regenerate one mole of MgSO₃ to sustain the cycle of absorption of SO₂ in the absorber.

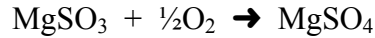


Typical soluble magnesium levels in this process range from 4,000-8,000 ppm.

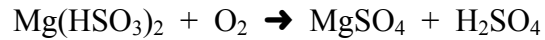
In the BSO process, soluble magnesium levels are elevated to 10,000 to 20,000 ppm. Soluble magnesium and sulfites increase accordingly to produce greater liquor alkalinity. As alkalinity increases, scrubber pH can be allowed to drop lower, making more of the soluble sulfites form bisulfite, a mild acid.

Oxidation and gypsum crystallization is performed at pH less than 6 external to the scrubber circuit thus allowing high pH (>6) and resulting high SO₂ removal conditions in the scrubber. The oxidation reactions are shown below.





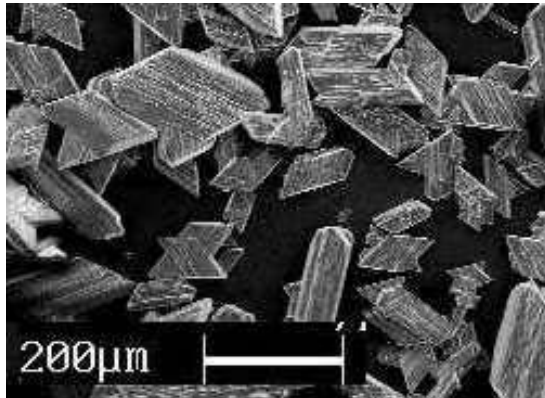
This ex-situ oxidation allows SO₂ scrubbing with lower power costs associated with lower L/G, fewer recycle pumps, and physically smaller size of scrubbers. This feature also makes retrofit of existing first and second generation FGD systems possible without much complication. The presence of bisulfite in slurry bled from the scrubber circuit is taken advantage of in the oxidation step, immediately downstream. Through oxidation of magnesium bisulfite, acid is produced and oxidizer pH drops to below 6, which is conducive to oxidation.



The gypsum produced from the BSO process has very consistent physical and chemical properties that make it quite suitable for modern high-speed wallboard production processes.

Note in Figure 2 the highly crystalline structure of the MEL FGD gypsum product compared to the calcium sulfite feed material of Figure 1.

Figure 2. SEM Image and Analysis for Typical Gypsum Product



ANALYSIS	TYPICAL VALUES
Moisture, wt %	10
pH	5-9
Purity, wt %	98-99
CaO, wt %	30-35
MgO	80-170 ppm
Chloride	20-40 ppm
Particle Size D50	<140 micron

Options for Magnesium Hydroxide Recovery and Benefits

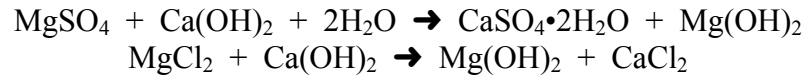
As mentioned earlier, MEL FGD using the BSO process can be implemented with or without magnesium hydroxide recovery. A utility might choose to include magnesium hydroxide recovery for the following reasons:

- In-plant uses of magnesium hydroxide might include neutralization of coal pile run-off water. Enrichment of the SO₂ reagent lime slurry to increase magnesium concentration.
- Raw synthetic magnesium hydroxide slurry was recently tested during two campaigns as a boiler injection additive to control SO₃ emissions⁴ at First Energy's Bruce Mansfield Plant, Unit 3.
- Mg(OH)₂ injection into the boiler may reduce problems associated with ash slagging. This may allow better fuel flexibility for the utility.

For plants where FGD wastewater treatment is required, recovery of magnesium hydroxide would substantially reduce load on the treatment plant.

Although the magnesium hydroxide slurry produced is typically 20-wt.% solids density, it may be cost competitive with commercial magnesium hydroxide slurry and especially caustic soda for commercial sale within a reasonable radius from the plant. Caustic availability has become an issue lately since caustic production has been curtailed, especially in the northwest US, due to escalating power costs.⁵

Magnesium hydroxide recovery in the process begins by taking the (magnesium) chloride purge stream that also contains high levels of soluble magnesium sulfate and feeding it to a regeneration tank. In the regeneration tank, calcium hydroxide from the lime slurry reacts with the oxidized liquor to form and precipitate gypsum and magnesium hydroxide solids.



Gypsum crystals that form in the regeneration tank are an order of magnitude larger than the co-precipitating magnesium hydroxide crystals. Hydroclones are used to exploit this size difference in separating gypsum from magnesium hydroxide.

The overflow streams from the primary hydroclones flow into the feed well of a magnesium hydroxide thickener. Product slurry density is 18 to 20-wt.%.

The underflow stream consists of most of the gypsum produced by the regeneration process and some residual magnesium hydroxide. This underflow stream is pumped to the oxidizer. Any residual alkali contained in this stream is consumed in the oxidizer.

Figure 3 is a flow diagram of the BSO process and Figure 4 shows the flow diagram of the BSO process with a magnesium hydroxide recovery circuit.

Figure 3. BSO Process without Magnesium Hydroxide Recovery

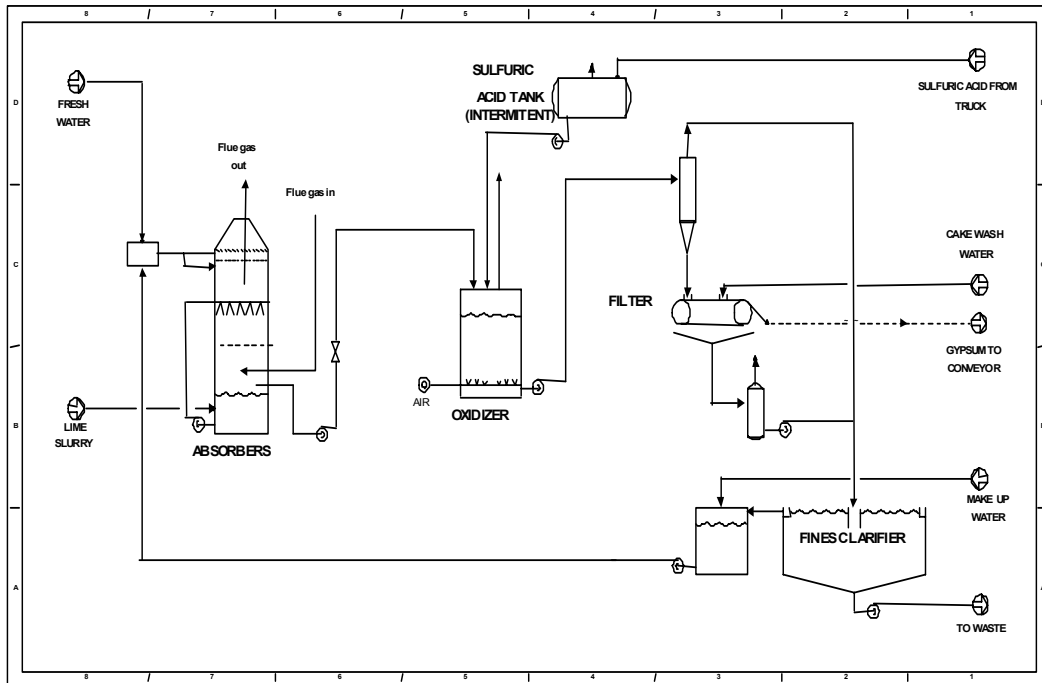
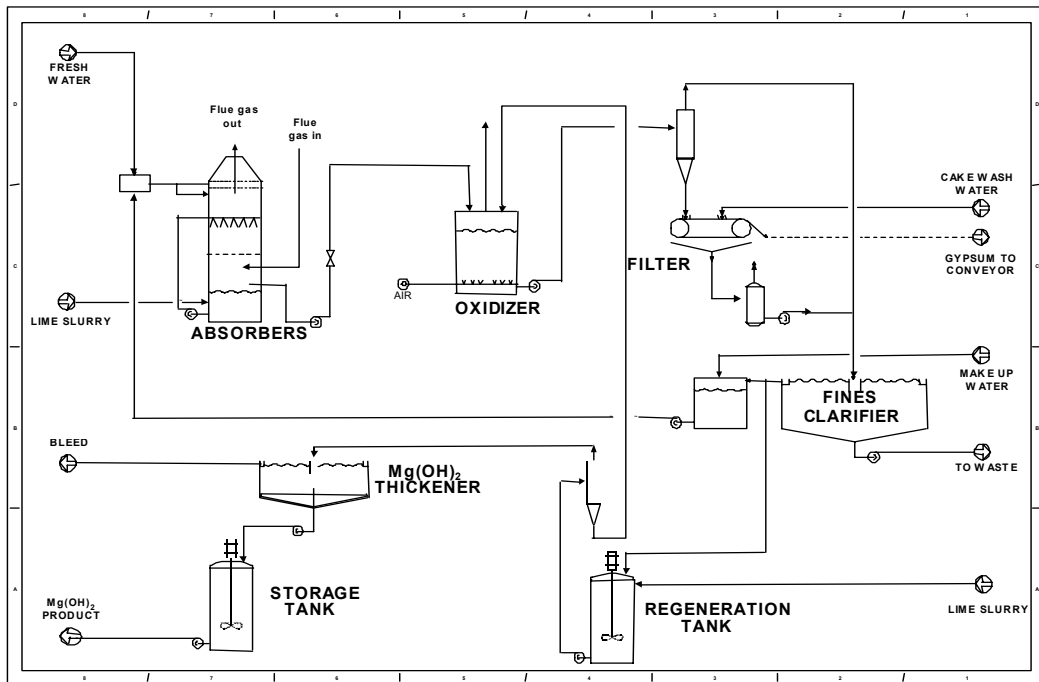


Figure 4. BSO Process with Magnesium Hydroxide Recovery



Retrofit and New Applications

Retrofit Applications

The recent applications of improved MEL FGD processes on commercial scale projects at the four different sites are primarily retrofits to pre-existing Thiosorbic[®] MEL FGD operations. The actual processes employed at each of these plants vary in process details and are adapted to the available equipment and other constraints specific to the plants. Although the four applications differ to some degree, three facilities are supplying gypsum to wallboard plants.

Working with one of our utility customers, tests were conducted at pilot scale for extended periods of time and a process was developed to oxidize the sulfite solids from a thickener underflow at the Mansfield station.¹ This plant needed to use feed from a scrubber operation where all of the fly ash is removed in the wet scrubber and the feed to the oxidizer therefore contained a large proportion of this fly ash. One of the process challenges was to minimize the coarse fly ash content upstream and fine fly ash content downstream of the oxidizer. Following the oxidizer circuit the fine ash was separated by using a Hydroseparator[®]. This plant has been routinely producing acceptable quality gypsum for the modern wallboard plant.

Another application was to take the oxidizer feed from the scrubber bleeds, which would otherwise be routed to a gravity thickener for settling. In this plant the scrubbers are supplied a mixed reagent of lime slurry and recovered $Mg(OH)_2$ from the back end of the process. The scrubber has a rich magnesium based chemistry to maintain high SO_2 removals. The oxidizer receives a stream of recycled gypsum seed crystals and these grow as the oxidation process progresses. This plant produces a high purity gypsum.

The third application of the oxidized MEL process is at the Zimmer station of CINergy. This 1,397 MW plus system uses the low pH bleed from the scrubber modules using a specially designed scoop placed strategically inside each of the scrubber modules. This plant also used a converted existing thickener underflow tank³ as the external oxidizer. This method of oxidizing the low pH bleed from the scrubber gives the most cost effective and simple oxidation system for process control purposes. Zimmer currently uses sulfuric acid to maintain oxidizer pH during scrubber operation upsets. These are the major unique design features of this plant.

In the case of retrofits from existing unoxidized MEL to oxidized MEL processes it is important to address the specifics of the existing plant equipment and operating needs to determine the optimum retrofit process modification. The most likely process for those applications where there is a need for minimizing the process control circuits and the retrofit costs is the bleed stream oxidation (BSO) with or without $Mg(OH)_2$ recovery.

If the plant can use the recovered $Mg(OH)_2$ at the station for 1) SO_3 control⁴ or for 2) other possible benefits (to be established) and 3) a greater fuel flexibility towards optimizing ash fusion properties in the boiler, a utility will have to seriously consider producing $Mg(OH)_2$. The high cost of commercial $Mg(OH)_2$ has prevented to date a number of high sulfur burning

utilities from considering this option. It is known that the minimization of SO_3 will let the air preheater exit temperature be lowered and not be limited by the high acid dewpoint; low SO_3 levels will also reduce the frequency with which the preheater needs to be cleaned.

New Applications

All of the retrofit oxidation MEL projects to date use an external oxidizer. The external oxidizer allows the advantage of running the scrubbers at conditions optimal for SO_2 removal while permitting optimization of the oxidizer operation independently from the scrubber circuit. Optimization of the oxidizer gives better quality control of the gypsum product.

Application of the oxidized MEL process today will most likely be the bleed stream oxidation process with or without $\text{Mg}(\text{OH})_2$ recovery. As mentioned earlier the BSO process has the minimum equipment needs and is easy to control. An external oxidizer allows flexibility.

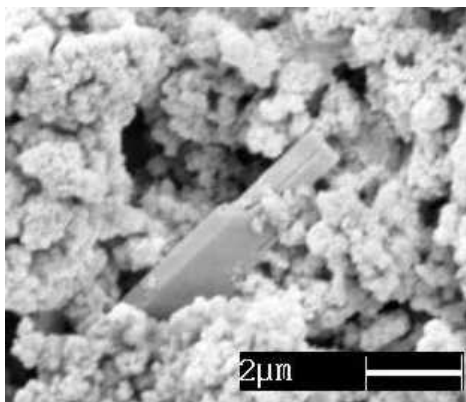
A byproduct $\text{Mg}(\text{OH})_2$ recovery system would become feasible if there is a need for $\text{Mg}(\text{OH})_2$ in the plant for:

- Boiler injection for SO_3 reduction (new SCR may dictate this need also)
- Treatment of water prior to disposal to reduce TDS and maintain desired pH control
- Boiler injection for better slag fusion properties (may allow greater fuel flexibility)

Production of $\text{Mg}(\text{OH})_2$ can be accomplished with minimal additional equipment. If quantities of $\text{Mg}(\text{OH})_2$ in excess of that available by using the conventional 3-7% MgO lime reagent is needed, this can be accomplished by increasing the reagent MgO content by blending the lime with dolomitic fines.

Figure 5 summarizes some of the characteristics of typical byproduct $\text{Mg}(\text{OH})_2$ recovered from the process. Note in the SEM photograph the fine size of the magnesium hydroxide compared to the gypsum crystal present.

Figure 5. SEM Image and Analysis for Typical Magnesium Hydroxide Product



Typical Magnesium Hydroxide Chemical Analysis	
MgO as $\text{Mg}(\text{OH})_2$, wt. %	55-80
Gypsum as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, wt. %	16-26
Inerts, wt. %	4-19
Total Suspended Solids, %	18-20
BET Specific Surface Area, m^2/g	50-55
Particle Size D50	2-4 micron

The oxidized MEL scrubber can achieve SO₂ removals of 99% with high sulfur coals at L/G substantially lower than the LSFO. The oxidized MEL scrubber will have a lower parasitic load of at least 0.5% less than the LSFO process.

Design Considerations

In addition to meeting ever more strict environmental regulations, recovery of salable byproducts that must meet customer minimum specifications necessarily complicates the FGD process and forces attention to operating and maintenance details in areas where neither was previously required. The magnesium-enhanced lime forced oxidation process has several circuits in its operation that require additional attention.

Scrubber Operation – Slurry density in absorber modules should be maintained at 15 wt.%. Mist eliminator wash water is a blend of fresh water and recycled FGD process water to maintain less than 50% gypsum saturation in the wash water.

Lime Slaking – Production of gypsum to meet customer specifications requires attention to lime quality and lime slaking. The main issue is minimizing grit production both to insure maximum lime utilization and minimal impact on gypsum quality, mainly pH. In a ball-mill or vertical mill slaker, grinding of grit to less than 200 mesh allows lime utilization to reach 99.9% and allows only a minimal amount of unreacted lime into the gypsum product.

Gypsum pH – The range of gypsum pH specified by wallboard producers is between 5 and 9. While gypsum from the MEL process achieves residual alkalinity (as CaCO₃) of 0.2 to 0.5 mg/g, corresponding to lime utilization of 99.9%, a portion of the alkalinity is present as CaO. This CaO can elevate gypsum pH. As a result, treatment of the filter cake with a minor amount of acid is sometimes required to neutralize the portion of the residual alkalinity that is CaO to bring gypsum into specification with respect to pH.

Water Management – Forced oxidation FGD plants requires special attention to balancing water use and loss within the plant because little water leaves in the gypsum product. Lime slaking, scrubber mist eliminators, and gypsum vacuum filters require fresh water that must be absorbed without placing an undue burden on waste water treatment plants while also limiting soluble chloride concentration within the process. Creative ways of balancing these competing demands begins in the engineering phase and continues through day-to-day operation. Examples of creative water use include reuse of process liquors by treatment and handling that reduces potential for both gypsum and calcium carbonate scaling, and minimizing water use by filters by having fresh water perform multiple tasks such as belt and cloth washing prior to filter cake washing.

Economics of MEL Process

Capital and Operating Costs - Estimating generic capital and operating costs is difficult since any particular station has unique requirements and situations to consider. EPA recently evaluated capital and operating cost of major FGD processes⁸ including the new MEL process. The capital and operating costs of the MEL process were competitive with LSFO.

Effect on Fuel Cost - Economic advantage can be taken of the MEL process by burning cheaper, higher sulfur fuel. The MEL process has a proven ability to handle flue gases from burning of high sulfur (>4%) coal. Historically, higher sulfur bituminous coal is usually lower in cost than lower sulfur bituminous coal.⁶ Recent coal pricing trends indicate an even more dramatic difference between moderate and high sulfur bituminous coal.⁷ Savings by burning of lower cost, high sulfur fuel could more than offset added FGD costs.

Utilities desire to be flexible with the type of fuel burned as environmental regulations and boiler operation allow. From the environmental aspect, it is necessary to maintain emission limits imposed by state and federal governmental agencies. Depending on the boiler type, higher sulfur containing fuels have ash slagging characteristics that may at least require a derate to remove deposits or be incompatible with the boiler altogether. The proven ability of BSO to scrub high sulfur fuels and the option of producing highly reactive magnesium hydroxide byproduct, with the potential for effective use as a boiler injection additive for slag control, gives the utility fuel flexibility that may not have been possible before.

CONCLUSION

Several years of R&D efforts by Dravo has culminated in the development of new MEL FGD options for the industry. These plants are now routinely producing gypsum and are supplying new wallboard plants. Dravo Lime Inc. is continuing its efforts to assist the plants in optimizing their operations and addressing any remaining operating and product quality related issues.

The new MEL FGD process retains all of the benefits of the Thiosorbic[®] lime based FGD process including high SO₂ removals with low L/G ratio due to the high liquor alkalinity, low parasitic load, and high system availability. In addition, it provides a high purity and consistent quality gypsum for use by the modern wallboard plants.

With fuel price increases in recent months and with utilities thus seeking lower cost coals, the BSO process with Mg(OH)₂ recovery may afford the utility a greater fuel flexibility. If a utility desires to make byproduct Mg(OH)₂ for in-plant use as a water treatment reagent and/or for the recently demonstrated boiler injection process in a coal-fired boiler for plume opacity control by capturing the SO₃⁴, the Mg(OH)₂ slurry production process is available and can be implemented with minimal additional equipment.

ACKNOWLEDGMENTS

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KEYWORDS

Magnesium-Enhanced Lime (MEL)
Flue Gas Desulfurization (FGD)
Magnesium Hydroxide
Scrubbers
Acid Rain
Forced Oxidation
Gypsum