

Marsulex AS Technology Significantly Cuts Power Generation Costs

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ABSTRACT

Utility deregulation is a reality. Successful generators of electricity will need to significantly lower bus bar cost of power by a creative combination of low cost fuel and the application of Marsulex Environmental Technologies' (MET's) patented Ammonia Scrubbing Technology. Because fuel constitutes the largest component of generation cost, substantial reductions can be achieved by firing low cost fuels such as high sulfur coal or petroleum coke. This option has been historically handicapped by sulfur dioxide emission limitations and related economics. MET's proprietary ammonium sulfate technology enables the use of lost cost, 5-7% sulfur fuels without the associated sulfur penalty. The MET technology can reduce generation costs by 25% or more on a typical coal-fired unit. In addition, this concept can also serve as the cornerstone of an SO₂ compliance strategy, or provide the winning edge in a bid for generation assets. This paper will outline this unique commercial and technical solution and provide economic examples of this cost-cutting strategy.

INTRODUCTION

Several factors have an impact on the cost of generation for utilities; namely, deregulation and compliance with the Clean Air Act amendments. Demand for coal is increasing, despite ever-increasing environmental regulations. Annual production at Wyoming's Powder River Basin coalfield has increased from 3 million tons in 1970 to more than 360 million tons in 2003. Nominal price increases are expected over the long term for most low sulfur coals, while prices for higher sulfur coals are expected to remain flat or to decline. The search for the lowest cost fuel, while being compliant with the CAA continues to be a major driver for utilities. Total annual SO₂ emissions will be reduced to 50% of 1980 levels (17.5 million ton reduction) by 2010.

In terms of the SO₂ allowance market, allowance pricing has risen from \$100-\$200 in the late 1990s to current pricing in the \$780-850 range (see Figure 1). Several factors have caused this upturn in pricing, most notably the high levels of generation in the East and Mid-West. These record-breaking levels of generation resulted in higher than anticipated SO₂ emissions that caused utilities to hold on to their allowances. Also, Phase II CAA requirements versus the possibility of having to comply with the

more stringent Clean Air Interstate Rule (CAIR) which would reduce SO₂ emissions below CAA limits for several states had many utilities holding on to their allowances and entering the market to purchase additional allowances. Allowance prices are projected to remain at current levels through 2009, to \$400-500 through 2012 and remain there through 2018.

The bottom line is that “business as usual” will not result in a decrease in generation cost or an improvement in dispatch order for the typical power plant. Creative solutions are required to position utility generators as the premier cost effective producers of electricity. MET is offering a fuel conversion solution to assist generators in significantly reducing cost. This paper will highlight important aspects of our proposed solution.

TARGET PLANTS

The four major components of added value for a successful fuel conversion project using MET’s patented technology include reduced fuel cost, increase load factor, conversion of ammonia to ammonium sulfate, and the sale of unused SO₂ allowances. The availability of high sulfur fuel at a low delivered price is one of the essential ingredients for a successful project. Petcoke, as an example, has been identified as a low cost, high sulfur fuel that can be burned in many boilers. In fact, there are several sites burning upwards of 100% pet coke for fuel. Given the relatively large volume of petcoke required for a major project, there were initial concerns about supply; however, as more refiners use crude with higher sulfur contents, both the quantity and quality (high sulfur content) of the petcoke increases. Use of high sulfur coal and/or oil as a fuel conversion option can also be quite lucrative.

Operating plants with a low dispatch factor driven by high fuel costs can improve their position in the dispatch order and increase the plant’s load factor. This can be a significant source of revenue for the project.

The conversion of ammonia to ammonium sulfate is another major source of revenue. Through the use of MET’s patented technology, every ton of ammonia utilizes generates approximately four tons of ammonium sulfate, the net effect of which leverages the price of ammonia by 70 – 400% based on current economics. MET’s process maximizes the use of sulfur in the flue gas plus the evaporative energy to achieve these economics (see Figure 2).

Based on a ten (10) year price scan of ammonium sulfate prices (See Figure 3), pricing of ammonium sulfate has continued to increase. And ammonium sulfate pricing has exhibited less volatility than ammonia. Several factors (see Figure 4)

contribute to the continuing demand for ammonium sulfate: 1) a non-volatile and non-explosive source of nitrogen, 2) its value as a nutrient for selected crops, 3) to replenish sulfur deficiency in soils, and 4) as an ideal product for blending and the addition of a slow-release polymer.

Revenue from the sale of SO₂ allowances has become a more significant component but is still the least in comparison to the three previous components.

In summary, the best opportunities to apply MET's AS technology will be found at power plants that match the following profile:

- High fuel cost
- Low load factor
- Proximity to navigable water, or good rail access for petcoke, ammonia and ammonium sulfate transportation
- Preferably in a location with high ammonium sulfate prices

MET'S SOLUTION

MET's patented, ammonia-based flue gas desulfurization process efficiently converts unwanted SO₂ into a high-value fertilizer byproduct. By combining this process with a fuel conversion to a low cost, high sulfur fuel, substantial savings can be realized. A typical 500 MW power plant currently firing compliance coal that switched to an 80% / 20% blend of petcoke and natural gas could realize fuel savings of \$.45 / mmBtu to \$.80 / mmBtu. Figure 5 provides an example of the savings possible with a 750 MW power station comprised of a 500 MW and a 250 MW unit. Current annual fuel cost of the units is \$83.5M, while the projected yearly cost utilizing the MET AS technology with a lower cost fuel is \$67.2M or a net reduction of \$16.3M annually. Savings can be even greater if SO₂ allowance generation savings are considered. The MET AS process, though slightly higher in capital cost than the traditional limestone FGD process, provides a revenue stream that can not only offset the initial capital cost of desulfurization but also provide an on-going source of revenue and allow the generator to realize fuel savings as well.

Process Chemistry

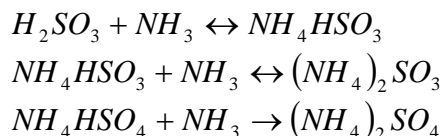
The chemistry of the production of ammonium sulfate from boiler flue gas is very similar to the chemistry of a limestone based reagent (see Figure 6). The removal of SO₂ from the flue gas occurs in the absorber spray zone where a spray of ammonium sulfate solution controlled at a pH range of 5.2-5.9, reacts with SO₂ to form ammonium

bisulfite/bisulfate in accordance with the following reactions:

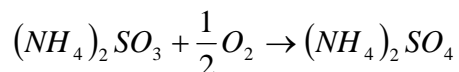
- (1) $SO_2 + H_2O \leftrightarrow H_2SO_3$
- (2) $H_2SO_3 + (NH_4)_2SO_4 \leftrightarrow NH_4HSO_4 + NH_4HSO_3$
- (3) $H_2SO_3 + (NH_4)_2SO_3 \leftrightarrow 2NH_4HSO_3$

In Reaction (1), SO_2 from the flue gas dissolves in water to form sulfurous acid and in Reactions (2) and (3) the sulfurous acid reacts with dissolved ammonium sulfate/sulfite salts in the solution.

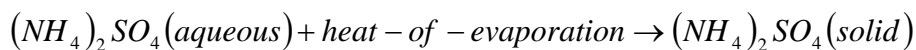
Ammonia is injected to the bottom of the reaction tank to neutralize the acidic species according to:



Oxidation air is injected into the bottom of the absorber to oxidize the sulfite to sulfate according to:



The ammonium sulfate solution is saturated and ammonium sulfate precipitates from the solution in a crystalline form due to chemical reaction and water evaporation into the flue gas. The heat of evaporation is supplied by the residual heat of the flue gas according to:



The salts in the absorber are either dissolved in an ionic form in the solution or precipitated in crystalline form. The product slurry is fully oxidized with the main component in the system being dissolved and crystalline ammonium sulfate salt. Nitrogen content of the product easily exceeds 20.5 wt%.

These reactions take place directly in the absorber vessel or in a prescrubber such as was the case at Dakota Gasification.

Dakota Gasification Plant Process Review

The process design for the ammonium sulfate process installed at the DGC plant is shown in Figures 7 through 10. Flue gas leaving three boilers is processed by a single train prescrubber and absorber (Figure 7). The flue gas enters the countercurrent prescrubber just above liquid level. The hot flue gas is contacted with a recirculating spray of ammonium sulfate slurry. In this vessel, the flue gas become saturated by evaporation of water from the recirculating slurry. The saturated flue gas leaves the prescrubber through a mist eliminator designed to remove slurry entrained in the flue gas.

After leaving the prescrubber, the flue gas enters a countercurrent absorber where it is contacted by a recirculating solution of subsaturated ammonium sulfate liquor. Ammonia is added with the oxidation air to maintain the recycle liquor at the desired pH to ensure that required SO₂ removal is achieved. The cleaned flue gas then passes through two stages of high efficiency mist eliminators to remove any entrained droplets. The primary purpose of the prescrubber is to separate the process function of SO₂ absorption and oxidation from product crystallization. Thermal energy from the flue gas is used to evaporate water from the prescrubber slurry as the flue gas is saturated. The evaporation of water causes crystallization of ammonium sulfate product and liquid level reduction in the prescrubber vessel. The subsaturated ammonium sulfate solution in the absorber is used to wash the prescrubber mist eliminator and maintain prescrubber vessel liquid level. As a result, subsaturated ammonium sulfate solution is introduced into the prescrubber where the excess water is evaporated and crystallization of product occurs. DGC was the first MET AS system installed. In subsequent projects, we have eliminated the prescrubber and SO₂ removal and evaporation and crystallization take place in the absorber.

The process steps of SO₂ absorption and oxidation take place in the dilute liquor phase in the absorber. In the absorber, SO₂ is removed and reacted with ammonia. Ammonia is introduced in gaseous form with the oxidation air. The ammonia is stored in a pressurized or refrigerated vessel and pumped as a liquid to a vaporizer. The vaporizer typically uses steam to vaporize the ammonia prior to introducing it into the oxidation air. Oxidation air is introduced into the absorber to oxidize the ammonium sulfate to ammonium sulfate. Ammonium sulfate solution (10-25 wt% dissolved solids) is bled from the absorber to the prescrubber to maintain the level in the prescrubber tank. Fresh makeup water required by the process is added to the absorber reaction tank to maintain tank level.

Slurry is bled from the prescrubber to a dewatering hydroclone, increasing the slurry density from 10 wt% to 35 wt% slurry (Figure 8). The purpose of the hydroclone is two-fold. First, the hydroclone is designed to dewater the slurry from the prescrubber to optimize the centrifuge feed slurry density. Secondly, the hydroclone separates the

fine particulate, primarily ash from the boiler, from the ammonium sulfate product thus maintaining product purity. The underflow of the hydroclone is directed via a diverter box to the centrifuge feed tank. The overflow of the hydroclone is diverted to the centrate tank.

In the event that the prescrubber solids density is lower than 10 wt%, the hydroclone underflow is combined with the hydroclone overflow and returned to the prescrubber via the centrate tank. The hydroclone underflow slurry is pumped to a series of basket centrifuges where slurry is dewatered to 97-98% solids. Centrifuges discharge the material immediately into a rotary drum dryer where heated air is passed over the crystals to further dry the material to less than one percent moisture. To maintain product purity, a portion of the hydroclone overflow can be diverted to a centrate filter press which captures the fine particulate matter, washes it, presses it dry and then discharges impurity solids at 50 wt% into a bin for disposal.

To maximize the byproduct value, the ammonium sulfate material in the storage silo must be converted from sugar-like crystals to larger granular crystals. To accomplish this, raw, unprocessed ammonium sulfate material is fed from the ammonium sulfate storage silo to the compaction system (Figure 9). In this system, fresh feed ammonium sulfate material is mixed with fine particles from the compaction process which is then recycled to the front of the process. The recycle and fresh feed ratio are monitored and controlled to produce an ammonium sulfate product with the hardest particle characteristics. After combining, fresh feed and recycle ammonium sulfate are mixed in a pug mill mixer to insure the recycle and fresh feed materials are fully mixed prior to compacting.

The material is fed to a compactor feed screw system that feeds the compactor rolls at high force. The material is forced between two rolls that compact the solids into a hard flake that is discharged into a flake breaker. The flake breaker crushes the large flakes into smaller pieces that can then be sized in a series of sizing mills.

These sizing mills use hammers and / or chains and specifically sized screens to generate a larger fraction of the material, between one and three millimeters in diameter. After being discharged from the mill, the particles are screened with all particles less than one millimeter being recycled to the beginning of the process. The particles greater than one millimeter are sent to a dryer where the residual moisture is dried to less than 1 wt%.

After being dried, the material is cooled to minimize the amount of moisture absorbed during storage and handling. The cooled product is screened in a two-stage screening process with material over three millimeters returned to the sizing mills and material less than one millimeter recycled to the beginning of the process. The final, on-size

product is transported to the storage dome. In this way, the size distribution of the granular product is controlled very closely. Figure 10 shows an overview of the plant with select design criteria.

SUMMARY

MET's patented and proven technology gives power generators a creative solution to reducing generation costs. The fuel conversion to substantially lower cost fuel combined with MET's technology permits most of the fuel savings to remain with the generator.

In summary, MET's fuel conversion solution provides guaranteed, long-term environmental compliance, requires no chemical or byproduct waste handling, and produces a high value ammonium sulfate byproduct resulting in significant power generation cost reduction.