

MARSH LANDING GENERATING STATION PROJECT MEMORANDUM

Date: February 3, 2010
To: Bay Area Air Quality Management District
From: Peter Landreth, Mirant & John Lague, URS
Subject: Revised Analysis of Expected Sulfate Formation at MLGS

This memorandum presents the development of a proposed permit limit for particulate matter (PM) emissions from the gas turbines of the MLGS and focuses specifically on the potential for the contribution of sulfate salt formation to PM emissions at the MLGS. Due to the general lack of existing data on PM¹ emissions from similarly equipped Siemens 5000F turbines (simple cycle, SCR and oxidation catalyst with dilution air), it has been necessary to analyze several types of information in order to determine an emissions limit that Mirant can be reasonably confident of achieving on an ongoing basis.

As Mirant has discussed with the Bay Area Air Quality Management District (BAAQMD or District), there are three principal components of overall PM emissions: (1) PM emissions at the turbine outlet (i.e., emissions resulting directly from the combustion of natural gas); (2) the PM contribution associated with the dilution air required for simple cycle turbines; and (3) the PM contribution of fuel gas sulfur conversion to ammonium salts. Based on discussions to date between Mirant (along with its consultant URS) and the BAAQMD, data regarding the first two of these components support reasonable assumptions of at least 8 lbs/hour of PM attributable to the turbine, and a 0.5 lbs/hour allowance for the contribution of PM associated with dilution air. This white paper elaborates on the third component, the potential for fuel gas sulfur conversion to ammonium salts, which URS described in a preliminary analysis provided to the BAAQMD on December 28, 2009. Since then, Mirant and URS have worked with Mirant's engineering contractors and potential catalyst vendors to prepare a more precise and accurate analysis of the expected contribution of sulfate formation to PM emissions. This analysis reflects the best information available to Mirant and its contractors on the issue of expected MLGS turbine emissions of PM.

Brief History of the Issue

Mirant's original MLGS application to the BAAQMD and the California Energy Commission (CEC) proposed a PM stack emission limit of 9 lb/hour. This value incorporated the Siemens guarantee of 8.0 lb/hour at the turbine exhaust outlet plus an additional 1.0 lb/hour to account for other factors, including:

- Fluctuations in the particulate loading of the dilution air that must be added to the turbine exhaust stream to lower its temperature to the operating range of the catalytic NO_x and CO emission controls downstream from the combustion zone (not required for combined cycle units like Russell City); and

¹ In this document, particulate matter emissions from the gas turbines are expressed simply as PM, with the understanding that virtually all emissions of particulate from such turbines will occur as both PM_{2.5} and PM₁₀.

- The potential contribution to PM stack emissions from sulfate salts that may be formed due to increased oxidation of SO₂ emissions to SO₃ in the stack gases of simple cycle turbines, as the less well-mixed turbine exhaust stream comes into contact with the catalyst material used in emission controls for NO_x and CO.

Having recently proposed a total PM emission limit of 7.5 lb/hour at similar Siemens turbines at the Russell City combined cycle facility, the District proposed a MLGS PM emission limit of 8.0 lb/hour, i.e., 7.5 lb/hour from the turbine combustion of natural gas plus 0.5 lb/hour to allow for the contribution of dilution air particulates, as described above. With a turbine assumption of 8.0 lb/hour and with the potential for higher sulfate particulate production in a simple cycle configuration, Mirant has raised concerns regarding the viability of this limit from a compliance standpoint as it relates to the MLGS. Accordingly, Mirant and BAAQMD have both conducted considerable research to obtain the best possible information upon which to base a reliable estimate of the expected particulate emissions that will be formed by various processes at MLGS and to set an associated permit limit based on that information.

Contribution of Sulfate Salts Converted from Fuel Gas Sulfur

The quantity of PM emissions from the MLGS turbine stacks will be significantly influenced by the ammonium sulfate salt formation from the SO₂ in the turbine exhaust created in the combustion process from the presence of sulfur in the fuel gas. A 2004 report commissioned by the California Energy Commission (CEC) examined variability in PM emissions from combustion turbines in California and found that “[p]erhaps the most significant single source of variation in measurements of PM from gas fired combustion systems is the potential for forming sulfate artifacts.”² (*emphasis added*) This report concluded that “artifact sulfate formation from conversion of gaseous SO₂ in the impingers can represent a major bias in measurement of condensed material. Depending on a variety of conditions, this artifact can increase the indicated level of condensable PM 10/2.5 and increase variability since the determining factors are neither well known nor controlled.”³ (*emphasis added*)

The CEC’s PM variability report supports the principle that sulfate formation can be a substantial contributor to PM emissions, but the CEC evaluated PM variability on a broad basis and did not focus specifically on the distinctions between combined cycle and simple cycle turbines as they relate to sulfate formation. Moreover, none of the combustion turbines considered in the CEC study comprised simple cycle turbines that are both equipped with SCR and that are designed to achieve a level of 2 ppm of CO. In fact, MLGS is the first facility of its kind that will involve those operational parameters.

² Lanier, W.S. and G.C. England, “Development of Fine Particulate Emission Factors and Speciation Profiles for Oil and Gas-fired Combustion Systems, Technical Memorandum: Conceptual Model Of Sources Of Variability In Combustion Turbine PM10 Emissions Data”(March, 2004) at p. 37.

³ Ibid, p. 16

As a general matter, some fraction of the SO₂ in the combustion exhaust stream of a gas turbine equipped with a SCR NO_x control system is oxidized to SO₃, which then combines with moisture in the exhaust stream to form sulfuric acid (H₂SO₄). The H₂SO₄ in turn reacts with ammonia slip from the SCR system to form particulate ammonium sulfate salts ((NH₄)₂ SO₄). According to Peerless Environmental Systems, the post-combustion catalytic equipment for control of NO_x and CO emissions is commonly designed to accommodate full conversion of SO₃ to particulates in the form of (NH₄)₂ SO₄. Thus, the important parameter in determining the potential for particulate formation from these reactions is the degree of conversion of the SO₂ formed in the turbine exhaust to SO₃. Because of their design to promote oxidation, CO catalysts account for most of this conversion in turbine systems equipped with catalytic emission controls.

Data from the Gateway Generating Station adjacent to the MLGS site, as well as an analysis of the nearby proposed Russell City Energy Center, indicate that in combined cycle applications, an SO₂ to SO₃ conversion rate of approximately 10% is a reasonable assumption. Mirant's preliminary analysis of potential sulfate contribution had simply focused on the relative NO_x catalyst inefficiency between combined cycle and simple cycle units as a proxy for similarly expected CO catalyst inefficiency, which indicates, in turn, a relatively higher rate of ammonium sulfate formation. Using this relative catalyst inefficiency approach and extrapolating from the benchmark assumption of 10% conversion for combined cycle units noted above, Mirant concluded that a reasonable assumption of SO₂ to SO₃ conversion would be 28%. However, Peerless Environmental Systems (Peerless)⁴, a prospective catalyst vendor for the MLGS, and Mirant's engineering contractors have cautioned that much higher conversion of SO₂ is to be expected for the MLGS units because SO₂ to SO₃ conversion is primarily a function of exhaust temperatures at the oxidation catalyst surface.

The MLGS, as a simple cycle gas turbine facility, has substantially higher exhaust temperatures than combined cycle applications at the CO catalyst⁵. Higher exhaust temperatures result in a higher conversion rate, resulting in significantly greater formation of sulfates than in combined cycle units, thus exaggerating the effect generally observed by the CEC in its report. The relative catalyst inefficiency described in Mirant's preliminary analysis is a function of the inherently higher temperatures (and corresponding introduction of dilution air) involved in simple cycle combustion, but focusing on the relationship between temperature and SO₂ conversion provides a more reliable model for predicting sulfate formation.

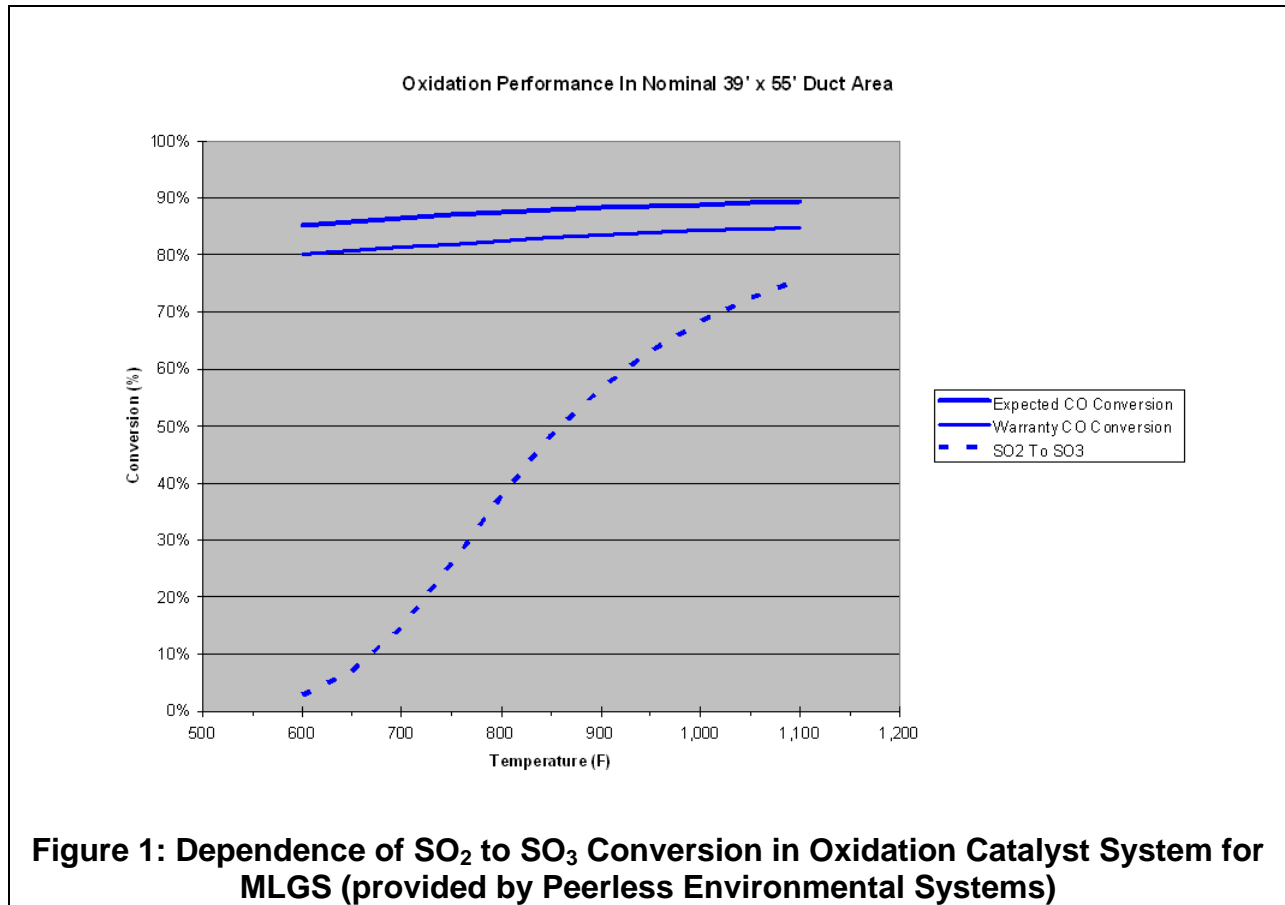
Mirant's preliminary analysis had assumed that the primary driver for incremental sulfate formation in simple cycle turbines above the level expected in combined cycle turbines

⁴ Peerless is a global leader in the design and manufacture of air emission reduction systems

⁵ Exhaust temperatures at the turbine outlet will be in excess of 1,100°F. Exhaust temperatures at the CO catalyst in the range of 850°F- 900°F are expected at MLGS, whereas in combined cycle applications exhaust temperatures at the CO catalyst are closer to the 600°F-650°F range.

was a function of the relative catalyst inefficiency at MLGS given that oxidation catalyst system in this case is being designed to achieve the extremely low CO emission level of 2.0 ppmv at 15% oxygen. Information subsequently provided by a prospective MLGS catalyst vendor (Peerless), however, indicates that, based on the performances parameters of the project (pressure drop, auxiliary load etc.), the required catalyst cross-section is roughly 39 feet by 55 feet, or ~2145 square feet. With this required cross-section, MLGS is virtually at the “minimum” manufacturing depth for CO catalyst. Accordingly, the same CO catalyst design will be required to achieve either 3.0 ppmv CO or 2.0 ppmv CO emissions levels (at 15% oxygen). Therefore, the primary driver for sulfate formation is the temperature-to- SO₂ conversion relationship. Analyzing potential sulfate formation specifically as a function of the critical relationship between temperature and SO₂ conversion provides a more precise and accurate projection of expected ammonium sulfate formation at MLGS.

There is a non-linear (exponential) relationship between exhaust temperature and SO₂ to SO₃ conversion. These relationships are shown below in Figure 1 (Peerless). This figure has been tailored by Peerless to reflect the specific expected operating conditions of the MLGS equipment and exhaust stream. The information provided by Peerless indicates that, based on the specific operational parameters (i.e. exhaust temperatures at the CO catalyst of 850°F – 900°F) associated with MLGS, an SO₂ conversion assumption in the range of 50% to 55% is reasonable. As noted below, this assumption is consistent with the observed rate of sulfate formation at the neighboring Gateway Generating Station as a function of exhaust stack temperature.



In order to estimate the potential for sulfate salts contribution to MLGS particulate emissions, it is first necessary to understand the sulfur content of the gas that will be delivered to the MLGS. The PG&E pipeline quality natural gas tariff states that the gas shall not contain more than 1 grain of total sulfur per 100 scf, which is the level BAAQMD has proposed as a BACT limit for fuel sulfur content for averaging times up to 24 hours. A value of 0.4 grains per 100 scf is proposed as the annual average limit.

An analysis of data on natural gas sulfur content at PG&E's Line 400/401 as measured at PG&E's analyzer in Burney, California was performed to evaluate the potential range and statistical properties of ammonium sulfate salt formation from combustion of this gas in the MLGS 5000 F turbines. This data set provided by PG&E consists of 26,210 hourly readings of total sulfur measured in grains per 100 scf from January 2007 to January 2010. The natural gas sulfur content for each hour of the data record was converted to an estimated ammonium sulfate salt contribution to PM₁₀ emissions from a single MLGS turbine as follows:

$$[(NH_3)_2SO_4 \text{ (lb/hr)}] = (\text{grains S/100 scf}) \times (1.0 \text{ lb/7000 grain}) \times (1 \text{ scf/1020 Btu}) \times 2202 \times 10^6 \text{ Btu/hr}) \times (64.07 \text{ lb SO}_2/32.02 \text{ lb S}) \times (\text{SO}_2 \text{ conversion rate}) \times (80.06 \text{ lb SO}_3/64.07 \text{ lb SO}_2) \times (132.14 \text{ lb (NH}_3)_2\text{SO}_4/80.06 \text{ lb SO}_3)$$

As noted previously, two different values for the SO₂ to SO₃ conversion rate were assumed to ensure that particulate formation from this mechanism would be addressed for the full range of conditions that have been suggested by various parties. Statistics of the measured natural gas sulfur content and the corresponding estimated hourly PM₁₀ emission rate contributed by ammonium sulfate salt formation during turbine operations are summarized in Table 1, which is followed by commentary on the results for different assumed SO₂ conversion rates.

Table 1
Statistics of Natural Gas Sulfur Content and Calculated PM₁₀ Emission
Contribution from Ammonium Sulfate Salt Formation
(n=26,210)

Statistic	Fuel Gas Total Sulfur Content (grains/100 scf)	Estimated PM Emissions Resulting from Conversion	
		50% SO ₂ →SO ₃ Conversion	55% SO ₂ →SO ₃ Conversion
Mean	0.216	1.374	1.511
Median	0.214	1.365	1.501
Mode	0.294	1.868	2.055
Standard Deviation	0.045	0.287	0.315
Minimum	0.014	0.086	0.095
Maximum	0.517	3.293	3.622
98th Percentile	0.341	2.172	2.389
95th Percentile	0.305	1.942	2.137

Results for 50% conversion The statistics in Table 1 for the 50% SO₂ to SO₃ conversion case, the minimum rate suggested by Peerless, indicate that the average sulfate contribution to stack PM emissions is approximately 1.37 lbs/hour, and the highest potential contribution of this mechanism is 3.29 lbs/hour for the maximum recorded fuel sulfur content at the Burney analyzer (0.517 gr/100scf). In addition, the 95th and 98th percentile values when the 50% conversion rate is assumed are 1.94 and 2.17 lbs/hour, respectively. A fuel sulfur content at PG&E's maximum allowed tariff rate of 1 grain/100 scf would yield a PM contribution from SO₂ to SO₃ conversion of 6.36 lbs/hr.

Results for 55% conversion When the assumed SO₂ to SO₃ conversion rate is raised to 55%, as suggested by the catalyst vendors, there is a proportional increase in the basic statistics in Table 1, and the PM contribution corresponding to the maximum recorded sulfur content in the Burney data set is increased to 3.62 lb/hour. The 95th and 98th percentile values for this case are about 0.2 lb/hour higher than those for the 50% conversion case. A fuel sulfur content at PG&E's maximum allowed tariff rate of 1 grain/100 scf would yield a PM contribution from SO₂ to SO₃ conversion of 7.00 lbs/hr.

These results confirm that the potential exists for average MLGS particulate stack emissions to be increased by 1.37 to 1.51 lb/hour due to the sulfur conversion process, with a significant risk of levels upwards of 2 lbs/hour occurring. Clearly, the contribution of this mechanism needs to be accounted for in the development of the MLGS emission limit for PM.

Available PM Source Testing Data from Other Gas Turbines

As noted above, there is very limited availability of PM emission testing data for Siemens 5000F turbines operating in simple cycle configuration, and no data at all have been located for units of this type that are equipped with SCR and CO catalyst systems. For this reason BAAQMD and Mirant have examined the available source test data from 5000F units in other operational configurations and for any other turbine models that have been permitted for simple cycle operation with SCRs and oxidation catalysts. No single test data set provides a true representation of the PM emissions from the MLGS units, but considered together, these data can provide useful insights and certain data can provide a basis for estimating these emissions in a manner that captures the combined contributions of all mechanisms of particulate formation. Specific data sets that have been identified are discussed below, and this section specifically addresses how the issue of expected sulfate formation at MLGS relates to these data sets.

LM6000 PM data. Data from 43 separate PM10 stack tests on LM6000 simple cycle turbines at 7 plants were collected and analyzed by BAAQMD. The District has indicated to Mirant that all of these units are operated in simple cycle and are equipped with SCR and oxidation catalyst systems. While the General Electric LM6000 is a much smaller gas turbine than the 5000F (about 450 MMBtu/hour versus 2200 Btu/hour HHV), this data set offers the advantage of providing total particulate emissions measurements at the stack for turbines that have at least nominally similar control equipment to that on the MLGS turbines. They can thus be used to determine emission factors (lbs PM per million Btu of fuel energy input) that can be used with the MLGS turbine fuel input to estimate its mass emissions. Since only total particulate data are included, the results incorporate the contributions of all PM-producing mechanisms, but do not distinguish their individual contributions.

Direct conversion of the LM6000 emission factors indicates that the MLGS units will have an expected average mass emission rate of 6.11 lb PM/hour/turbine. However, the data for 10 of the 43 individual tests (23%) translate to emission rates of 8.5 lb/hour or higher, 6 tests (14%) are above 9 lb/hour and 4 tests (9%) are above 10 lb/hour. In addition, according to Peerless, the operating temperatures for the LM6000 oxidation catalyst are lower than the catalyst system for the 5000F turbine. Data from LM6000 projects permitted by URS shows temperatures at the turbine exhaust of these units are typically around 850 deg F. In addition, the LM6000 source test data were collected at facilities that were permitted when the prevailing simple cycle BACT level for CO was at least 4 ppmv at 15% O₂ and in some cases 6 ppmv. Accordingly, in light of the relationship between temperature and SO₂ to SO₃ conversion, the LM6000 data likely reflect a substantially lower rate of SO₂ conversion to SO₃ and a corresponding lower

production of the sulfates component of PM than would be expected to occur with the MLGS simple cycle 5000F units. The LM6000 data therefore likely underestimate expected comparable MLGS emissions.

Renaissance Power LLC PM data. A report on 2008 stack testing conducted on four 5000F simple cycle turbines at the Renaissance Power LLC facility in Michigan provides PM emission data for turbines of the same class as those of the MLGS. However, the Renaissance units are not equipped with SCR or oxidation catalyst systems. Accordingly, the primary value of this dataset is in the opportunity it provides to evaluate the basic turbine PM emission assumption of 8.0 lbs/hour at the 5000F exhaust outlet. These data reflect no contribution from ambient particulate loading in dilution air or the enhanced SO₂ to SO₃ conversion and excess sulfate particulate production expected for units with oxidation catalysts. The Renaissance results are summarized in Table 2 below.

Table 2
Source Test PM Data for 5000F Turbines at Renaissance Power LLC

Unit	Lb/hr PM	Lb/MMBtu PM
Turbine 1	7.91	0.00440
Turbine 2	8.04	0.00443
Turbine 3	6.19	0.00346
Turbine 4	5.44	0.00366

These data confirm that the 8.0 lb/hour assumption for the 5000F units at the exhaust outlet is a reasonable estimate of probable PM emissions resulting from the turbine combustion process, and that additional allowance needs to be made for the contributions of dilution air and sulfur conversion processes, since these are not reflected in the Renaissance test data. Note that the lb/MMBtu values derived for all four of these tests exceed the value of 0.0034 adopted by the BAAQMD in the Russell City combined units proceeding.

Gateway Generating Station H₂SO₄ and (NH₄)₂SO₄ stack data A series of three stack tests was conducted in January 2009 on the two General Electric 7FA gas turbines of the Gateway Generating Station adjacent to the MLGS site. These tests provide measured stack concentrations of SO₂, H₂SO₄ and (NH₄)₂SO₄ for these turbines operating in combined cycle mode. BAAQMD provided Mirant with an analysis of this data set, the highlights of which are summarized below:

- The average conversion of SO₂ to H₂SO₄ determined by the tests was 7.3 percent for the Gateway turbines and the average hourly mass emission rates of H₂SO₄ for the two units were 0.166 lb/hour and 0.154 lb/hour.
- The average conversion of SO₂ to (NH₄)₂SO₄ determined by the tests was 5.67 percent for the Gateway turbines and the average hourly mass emission rates of (NH₄)₂SO₄ for the two units were 0.161 lb/hour and 0.173 lb/hour.
- Assuming that the same SO₂ conversion rates shown above for the combined cycle Gateway generating units are also applicable to the MLGS simple cycle

units, BAAQMD calculated MLGS H_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$ emission for different natural gas sulfur contents, as shown in Table 3 below.

Table 3
MLGS H_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$ Emission Rates Predicted by BAAQMD Based on Source Tests on Gateway Generating Station Combined Cycle Turbines

Total Gas Sulfur Content (Grains/100 scf)	Basis for Sulfur Content	Predicted MLGS Emission Rate of H_2SO_4 (lbs/hour)	Predicted MLGS Emission Rate of $(\text{NH}_4)_2\text{SO}_4$ (lbs/hour)
0.25	Near the average recorded during Gateway tests	0.17	0.18
0.713	Maximum PG&E value over last four years	0.49	0.51
1.00	Maximum allowable value in gas from PG&E	0.69	0.72

These data show that at least for the Gateway combined cycle units, approximately equal production of H_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$ mass emission rates were observed at the stack exit, i.e., full conversion to sulfate salts did not occur in the stack. The combined production of both compounds was only about 0.35 lb/hour for a relatively typical fuel sulfur content of 0.25 grains/100 scf. However, the total corresponding to the historical high gas sulfur content during the last four years (0.713 gr/100 scf) is 1.0 lb/hour and the value for the peak allowable sulfur content of 1 grain/100 scf is about 1.4 lb/hour.

Considering that these results are based on the application of SO_2 conversion rates derived from stack tests on combined cycle units, and recalling the strong temperature dependence of the conversion rate (Figure 1), the corresponding contribution of this mechanism to particulate emissions at MLGS should be well above the levels indicated in Table 3. In fact, the observed rate of sulfate contribution to PM emissions at the Gateway Generating Station in Table 4 is consistent with the temperature curve provided by Peerless in Figure 1 and supports the fact that a much higher conversion rate of 50-55% SO_2 conversion at MLGS is reasonable given the expected exhaust temperature at the CO catalyst face. Table 4 below provides a comparison of the Gateway sulfate formation data to the projected sulfate contribution rates at MLGS in Table 1 (based on the statistical analysis of sulfur content and the assumptions provided by Peerless) and illustrates the incremental contribution of sulfates to PM emissions at MLGS relative to Gateway (and to comparable combined cycle facilities) assuming the mean sulfur content of around 0.25 grains/100 scf.

Table 4
Incremental Sulfate Contribution at MLGS Relative to Gateway Generating Station

	Assuming 50% MLGS conversion (lbs/hour)	Assuming 55% MLGS conversion (lbs/hour)
Measured Gateway (NH ₄) ₂ SO ₄ Concentrations	0.17	0.17
MLGS(NH ₄) ₂ SO ₄	1.37	1.51
Increment (NH ₄) ₂ SO ₄	1.2	1.34

Conclusion

Analyzing the potential for sulfate contribution to PM emissions at MLGS as a function of the relationship between exhaust stack temperature and SO₂ conversion indicates that expected levels of sulfate formation will be substantially higher than initially anticipated. The information provided by Peerless indicates that this contribution would typically range from 1.37 to 1.51 and could range well above 2 lbs/hour. Accordingly, the MLGS PM limit should recognize and account for the incremental risk of sulfate formation in simple cycle units.