**UNITED STATES ENVIRONMENTAL PROTECTION AGENCY**
REGION 4
ATLANTA FEDERAL CENTER
61 FORSYTH STREET
ATLANTA, GEORGIA 30303-8960

JAN 18 2008

Trina Vielhauer, Chief
Bureau of Air Regulation
Florida Department of
Environmental Protection
Bob Martinez Center
2600 Blair Stone Road
Tallassee, FL 32399-2400

RECEIVED
JAN 25 2008
BUREAU OF AIR REGULATION

Dear Ms.Vielhauer:

Thank you for the opportunity to review the proposed Best Available Retrofit Technology (BART) evaluation for Mosaic Fertilizer, LLC-New Wales Plant.

Enclosed are our comments on the Mosaic Fertilizer, LLC-New Wales Plant document. Please note that we may have additional comments on this draft.

We appreciate your transmittal of this package for our consideration. If you have questions regarding this letter, please contact Heidi LeSane of the Region 4 staff at (404) 562-9074.

Sincerely,

Richard A. Schutt
Chief
Air Planning Branch

Enclosures

# Mosaic Fertilizer, LLC-New Wales Plant Comments

## Cesium promoted catalysts in Sulfuric Acid Plant

SAP1,2,3 BART - These three units are double contact acid plants which were permitted for increased production to from 2900 to 3400 tons/day of 100% Sulfuric Acid in 2002. Proposed BART for is 3.5 lbs/ton of acid produced. It is not stated in the Technical support document whether these units presently use a Cesium promoted catalyst to any extent. Cesium promoted catalysts were introduced in the late 1990's to early 2000's timeframe. They extend the temperature range over which the catalyst is active. This increases the conversion efficiency by about 50%. They are designed to directly replace the phosphorus promoted vanadium pentoxide catalysts in use. So, in many cases, other than catalyst replacement costs, the changes necessary to implement this technology are minimal even though this is a single contact acid plant.

It is possible that the plant switched to Cesium promoted catalysts on these units for the purpose of increasing production while maintaining emission rates at NSPS levels. Several plants have gotten BACT determinations in the past few years for expansions while meeting the NSPS based 3.5-4.0 lbs SO2/ton of Acid produced range rather than achieving the 1.5-2.5 lbs SO2/ton of acid produced capability the new catalyst provides. Typically when this occurs the unit has increased the concentration of SO2 entering the unit without a commensurate increase in % Oxygen, allowing these units to increase production 10-20% while maintaining an NSPS based compliance limit of 3.5-4.0 lbsSO2/ ton of acid produced. Although these units have the right technology they have not been optimized to lower emissions. These plants should determine the feasibility of the process modification necessary to bring the operating parameters (temperature, %SO2, % Oxygen) to the optimum ranges. This can be done by adjusting inlet SO2 concentrations or adding air either in the initial feed or in the final stage(s) where the Cesium catalyst is introduced. If the facility presently uses Cesium promoted catalysts, this process modification should be identified as an available technology. This evaluation should include a cost effectiveness evaluation (*i.e.,* dollars/ton of SO2 removed) of operating the cesium catalyst at optimum oxygen levels resulting in lower emission limits (*e.g.,* 2.0 lb SO2/ton acid).

## Enforcement Issues

Top-down evaluations at sulfuric acid plants are somewhat complex due to the fact that, when dual absorption is used, the sulfuric acid plant converter is essentially its own control device. Because of this, the way the acid plant is designed and operated has a significant effect on the achievable emission rate. EPA's *Guidelines for BART Determinations* in Appendix Y to 40 CFR Part 51 provides guidance for both add-on control equipment or inherently lower polluting process equipment that have a wide range of emission performance levels:

> Many control techniques, including both add-on controls and inherently lower polluting processes, can perform at a wide range of levels. Scrubbers and high and low efficiency electrostatic precipitators (ESPs) are two of the many examples of such control techniques

that can perform at a wide range of levels. It is not our intent to require analysis of each possible level of efficiency for a control technique as such an analysis would result in a large number of options. It is important, however, that in analyzing the technology you take into account the most stringent emission control level that the technology is capable of achieving. You should consider recent regulatory decisions and performance data (e.g., manufacturer's data, engineering estimates and the experience of other sources) when identifying an emissions performance level or levels to evaluate.

In performing a BART evaluation at a sulfuric acid plant choosing to use dual absorption technology (or already equipped with this technology), the combination of a variety of factors including the use of cesium catalyst, catalyst loading, installation of a 5th catalyst bed, and improving the $O_2/SO_2$ ratio should be considered. Furthermore, several different scrubber options should also be considered. Any decision to eliminate a scrubber based on cost-effectiveness should present the average and incremental cost effectiveness of each type of scrubber system.

Cesium Catalyst

Vanadium pentoxide catalyst promoted with cesium in lieu of potassium was first marketed for sale in the late 1990's. Cesium catalyst is capable of reducing emissions in any contact process sulfuric acid plant. In 3x1 dual absorption plants, replacing the 4th bed of conventional catalyst with the current generation of cesium catalysts will reduce emissions approximately 65%, all other things being equal before and after. This is an extremely cost-effective way to reduce large amounts of $SO_2$ emissions. However, instead of using cesium catalyst to reduce pollution, some have used it as a means to increase sulfuric acid production by running a sulfuric acid plant under very poor conditions while still maintaining compliance emission limits only slightly lower than the 4.0 lbs/ton standard that was developed in the 1970s (well before the advent of cesium catalyst).

At least 20 sulfuric acid plants nationwide are (or will be) required to meet emission rates less than 2.5 lbs/ton. Many of these plants utilize dual absorption and cesium catalyst, and many use a scrubber. At least one plant uses both. A table of these plants is attached. Both major cesium catalyst vendors, MECS and Haldor Topsoe, consistently advertise that emission rates of 100 ppm (approx. 1.5 lbs/ton) are achievable in the 3 x 1 dual absorption configurations and will provide a guarantee for these rates. Additionally, FDEP did not discuss the cost effectiveness of scrubber systems in its technical BART analysis.

Factors to be Considered in Top-Down Analysis

The following operating and design factors should be considered when determining BART for any dual absorption contact process sulfuric acid plant:

1. **The $O_2/SO_2$ ratio:** The $O_2/SO_2$ ratio is the ratio of oxygen to sulfur dioxide heading into the converter. The higher this ratio, the higher the conversion as the greater availability of excess oxygen improves reaction equilibrium. The lower this ratio, the higher the plant's production rate because of the higher sulfur loading. Dual absorption sulfuric acid plants generally run at an $O_2/SO_2$ ratio of 0.8 or greater. This is equivalent to a converter inlet $SO_2$

concentration of 11.5%. Applicants required to meet BART should not be able to justify a higher emission limit than 1.5 lbs/ton because of plans to operate at an $O_2/SO_2$ ratio less than 0.81. Furthermore, applicants should not be able to justify a higher emission rate of 1.5 lbs/ton by arguing that such a limit would inhibit acid production. This is a false choice. The acid production rate can be maintained while reducing the $O_2/SO_2$ ratio by increasing the airflow to support the desired acid production rate. This can be done by reducing plant pressure drop or by increasing blower capacity.

2. **Catalyst loading:** This value is generally expressed in L/TPD and it is the ratio of catalyst in the converter to the productive capacity of the plant. In any sulfuric acid plant, there must be sufficient catalyst to assure proper conversion of $SO_2$ to $SO_3$. The higher this ratio, the lower the emission rates that is achievable in the acid plant. Applicants meeting BART requirements should analyze the cost of increasing catalyst loading to at least 220 L/TPD. Many converters have room for additional catalyst. However, a converter replacement may be necessary. If the existing converter is 20 years old or more, replacing the existing converter with a new converter that allows for more catalyst loading is particularly cost effective. The useful life of a converter is 20 to 30 years, and a converter over 20 years old is due for a replacement in the near future. In this case only the cost delta between a replacement of a converter with a larger volume (and/or a 5th bed) and a replacement in-kind should be considered.

3. **5th Catalyst Mass:** 5 bed converters, utilizing the 3x2 arrangement are frequently used in Europe and elsewhere overseas. At least three sulfuric acid plants in the US are equipped with a 5th bed. In Germany, all sulfuric acid plants are required to be equipped with 5 catalyst beds. A 5th mass can be installed in a separate vessel from the existing converter or incorporated into a single converter shell. A 5th mass will certainly allow for emission rates below 1.5 lbs/ton with ample compliance margin. Any BART evaluation should consider installation of a 5th mass.

4. **Replacing Heat Exchangers:** Heat exchangers in poor condition can make compliance with $SO_2$ emission limits more difficult either by increasing pressure drop or by leaking $SO_2$ rich gas into a leaner $SO_2$ stream. If necessary, replacement of heat exchangers should be considered in any BART evaluation. Replacing heat exchangers near the end of their useful life is particularly cost effective.

Also, a variety of scrubber options should be considered. In at least one case in the US, a dual absorption sulfuric acid plant is equipped with a tail gas scrubber to achieve an emission rate of 0.2 lbs/ton. This control practice is more common in Europe. While these options may be eliminated on the basis of incremental cost effectiveness, they should be considered, and the findings should be presented in the BART determination. Furthermore, these options should be evaluated particularly closely if the applicant has a strong desired to run at a low $O_2/SO_2$ ratio or with low catalyst loadings.

1. **Installation of an alkali scrubber:** Alkali scrubbers have been proven effective at controlling emissions from sulfuric acid plants to very low levels. Sodium, ammonia, and limestone based reagents can be used to remove $SO_2$ from a gas stream. When using sodium,

the scrubber effluent will be sodium bisulfite, which can be sold as a product. When using ammonia, ammonium sulfate can be sold as a product or used to for grade control in the production of phosphate fertilizer. When using limestone as a reagent, a solid gypsum material can be recovered and sold as a product.

2. **Installation of a regenerative scrubber:** Amine based regenerative scrubbing systems have been proven effective at controlling emissions of sulfuric acid plants down to 50 ppm. Such systems are specifically marketed to sulfuric acid producers under the trade name Cansolv. These systems do not generate any waste stream and are easily able to meet emission rates of 1.0 lbs/ton or less.

3. **Installation of a hydrogen peroxide scrubber:** Hydrogen peroxide will react directly with $SO_2$ in the tail gas to form sulfuric acid. Sulfuric acid recovered from the scrubber can be blended with outgoing product. There is no waste stream created by such a scrubber.