Bay Area Air Quality Management District

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Bay Area 2010 Clean Air Plan
Control Measure SSM 8
BAAQMD Regulation 9, Rule 14:
Petroleum Coke Calcining Operations

DRAFT Workshop Report
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WORKSHOP REPORT

Draft Regulation 9, Rule 14

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I. INTRODUCTION

This workshop report provides preliminary information regarding the intended adoption by the Bay Area Air Quality Management District (BAAQMD or Air District) of a new regulation that would control sulfur dioxide (SO_2) emissions from the Phillips 66 petroleum coke calcining plant in the town of Rodeo. The draft rule would apply generally to petroleum coke plants; however, Phillips 66 currently operates the only such plant within the jurisdiction of the Air District. This facility, commonly referred to as the "Carbon Plant," operates two rotary kilns in its calcining operation. The Carbon Plant is the single largest emitter of SO_2 in the Air District's air basin. SO_2 emissions are a public and environmental health concern and also contribute to particulate matter formation in the atmosphere.

Petroleum coke, often referred to as "green coke," is a black solid residual from various petroleum refining processes. In a calcining operation, green coke is sent through a heated rotary kiln to drive off contaminants in order to produce a purer form of carbon. Green coke tends to contain sulfur in addition to other contaminants. As the heat in the calcining process drives off contaminants from the coke, gaseous emissions are produced including SO_2. When the Carbon Plant calcines green coke under normal conditions, meaning fully operational conditions, the total sulfur dioxide emissions are approximately 3.4 tons per day. The purpose of this control measure is to reduce SO_2 emissions which in turn will reduce the formation of particulate matter.

In Control Measure SSM 8 of the Bay Area 2010 Clean Air Plan, the Air District committed to investigating the potential for reducing SO_2 emissions from petroleum coke calcining plants.[1] This rule is part of the Air District's strategy to reduce emissions from Bay Area petroleum refineries. The South Coast Air Quality Management District (SCAQMD) and the San Luis Obispo County Air Pollution Control District (SLO APCD) are the only air districts in the state that have adopted rules that specifically regulate SO_2 emissions from petroleum coke calcining operations. Their rules require an 80% emission reduction.[2, 3] The ConocoPhillips calcining facility within the SLO APCD jurisdiction is no longer operating. Thus, the Carbon Plant is one of only two petroleum coke calcining facilities operating in the State of California.

The draft new rule, Regulation 9, Rule 14: Petroleum Coke Calcining Operations, would apply only to the Carbon Plant as it is the only petroleum coke calcining facility currently operating in the Bay Area. Equivalent to the emission limits currently in effect in the SCAQMD and SLO APCD, Regulation 9, Rule 14 proposes an SO_2 mass emission limit of 50 pounds per hour that would apply to each kiln. Regulation 9, Rule 14 would go into effect twenty four months after the date of adoption. Staff estimates SO_2 emissions at the Carbon Plant will be reduced by 2.45 tons per day.

Cost-effective technologies that can achieve the draft SO_2 emission limit required by Regulation 9, Rule 14 are readily available. Such technologies are used in the petroleum coke calcining industry and other industries such as coal fired power plants and Portland Cement manufacturing facilities. The Carbon Plant has SO_2 control equipment currently in operation, but the degree to which SO_2 emissions are controlled does not meet the emission limit the Air District is considering for this rule.

The Air District is publishing this report to outline and explain the draft rule to the public, the affected facility, and any other interested persons. This report includes a description of the petroleum coke calcining industry in the Bay Area, an overview of petroleum coke calcining operations, and an explanation of how SO_2 emissions can be minimized. The report then describes the draft rule that staff is proposing, and estimated emission reductions and costs.

The Air District will hold a public workshop to discuss the draft rule and invite participation in the workshop and written comments on any aspect of the proposal. When staff finalizes the draft rule and staff report, they will be submitted for consideration by the Air District's Board of Directors.

II. BACKGROUND

A. *Petroleum Coke Calcining Operations in the Bay Area*

The Carbon Plant is currently the only petroleum coke calcining facility operating in the Bay Area. It is one of only two such facilities in the State of California. The other facility is in Southern California. The Carbon Plant processes green coke from the Phillips 66 San Francisco Refinery to purify it and sell it to industry. The facility commenced calcining operations with a single kiln in 1960. A second kiln was added to the facility in 1968.

The Carbon Plant sells the majority of its calcined coke to a single company that uses the refined coke to produce titanium dioxide – a photocatalyst that is commonly used to manufacture white pigments that are incorporated into a wide range of applications including skincare, plastics, food coloring as well as paint and coating products.[4] A photocatalyst is a material that alters the rate of a chemical reaction when exposed to light.[5]

B. *Petroleum Coke and Calcining Operation Overview*

Petroleum Coke

Petroleum coke is a carbon by-product that remains from petroleum refining processes. It is a black solid residue that results from the thermal processing of petroleum derived feedstocks, tar, pitch, or vacuum tower bottom blends that have been cracked or otherwise processed in cokers to remove low boiling fractions. Coke consists mainly of carbon (90- 95%) and is created by heat-treating the residual oil (more accurately described as tar) to a temperature high enough to polymerize it to form a non-melting solid carbon.

Coke is used as a feedstock in coke ovens for the steel industry, for heating purposes, for electrode manufacturing, and for the production of chemicals. The two most common types of coke are "green coke" and "calcined coke." Coke, as it is removed from the petroleum coking process, is referred to as "green coke." Green petroleum coke may contain approximately 15% to 20% residual hydrocarbon materials. Such hydrocarbons are compounds that do not polymerize in the coke cracking process and cannot be removed from the coke substrate due to process limitations. Thus, green coke is calcined to remove hydrocarbons and other impurities to make it a marketable product.

Calcining Process

Calcined petroleum coke is manufactured by heating green coke in a rotary kiln to a temperature that ranges between approximately 2200 - 2500 degrees Fahrenheit. This roasting process combusts virtually all of the residual hydrocarbons and also removes moisture from the coke. The coke's crystalline structure is refined and thus enhances the coke's physical properties such as electrical conductivity, real density (an indicator of calcined coke porosity), and oxidation characteristics. The final calcined product contains only a trace of volatile matter and sulfur content ranging from 0.3% to 6% depending on the original product used to generate the coke. Figure 1 is an image of calcined petroleum coke.

Figure 1: Calcined Petroleum Coke

Image Source: Carbon Plant

A rotary kiln is a long, refractory lined cylindrical device that rotates on its own axis and drives off contaminants from the green coke by bringing the contaminants into direct contact with heated gas. As the petroleum coke slides down the rotating kiln it flows counter-current to the rising hot combustion gas produced by burning natural gas. Figure 2 is an image of a coke calcining kiln at the Carbon Plant.

Figure 2: Calcining Kiln

Image Source: Carbon Plant

Sulfur Dioxide

Sulfur dioxide (SO_2) belongs to the family of sulfur oxide gases (SO_X). Sulfur is prevalent in green coke as well as raw materials such as crude oil, coal and metal ores. SO_X gases are formed when fuels containing sulfur, such as coal and oil are burned. SO_2 dissolves in water vapor to form acid and interacts with other gases and particles in the air to form sulfate particles and other products that can be harmful to people and the environment. SO_2 and the pollutants formed from SO_2 can be transported over long distances and deposited far from the point of origin, thus, air quality impacts of SO_2 are not confined to areas where it is emitted. The sulfur emissions also contribute to ambient $PM_{2.5}$ pollution through the formation of sulfate particles. In addition to SO_X emissions, other pollutants are emitted from the Carbon Plant’s calcining operation, including nitrogen oxides and fine particulate matter.

Scientific evidence links short-term exposures to SO_2 with various respiratory problems as well as the exacerbation of existing cardiovascular disease.[6] Emissions that lead to increased SO_2 concentrations generally lead to the formation of other SO_X gases, thus, the control of SO_2 can be expected to reduce exposure to all SO_X gases. This has the co-benefit of reducing the formation of sulfate particles which pose significant health threats. The small particles that are formed from sulfur dioxide can penetrate deeply into the lungs and worsen respiratory diseases such as emphysema and bronchitis. Fine particles can also worsen existing heart disease.[7]

III. TECHNICAL REVIEW

The emission limit requirements in Regulation 9, Rule 14 would apply to a single facility: the Phillips 66 Carbon Plant located in Rodeo, California. This facility is a top emitter of SO_2 and its current level of control for this pollutant is not consistent with Best Available Retrofit Control Technology (BARCT). More detail regarding this facility is provided in Section B of this technical review.

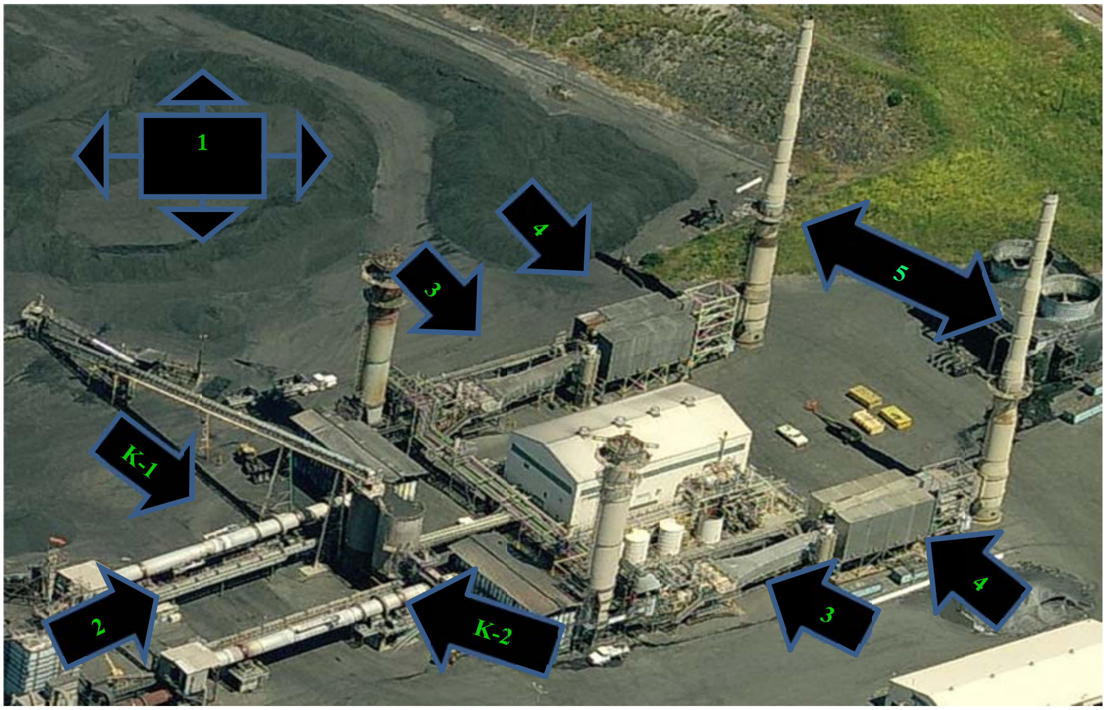
A. Emissions Inventory

The Carbon Plant is the largest emitter of SO_2 in the Air District's air basin according to the 2013 emissions inventory. The Carbon Plant emits approximately 3.4 tons per day (TPD) of SO_2 emissions combined from both kilns when they are fully operational.

B. Plant Description

The Carbon Plant calcining operations are illustrated in Figure 3. The first step in the calcining process is the transfer of green coke via a conveyor belt from the green coke stockpile (1) into the kilns marked as (K1) and (K2). The coke is thermally treated in the kilns (2) and is then rerouted to a storage area while the acid gas stream containing SO_2 flows through a heat recovery system and into exhaust flues (3) where dry sorbent material is injected to mix with the SO_2. The sorbent/acid gas particles flow into a baghouse (4) and attach to modules – a series of bags constructed of a filter fabric. As the particles layer upon themselves over several hours, they form a paste on the modules. Approximately every twelve hours, the baghouse modules are pulsed (shaken), causing the paste to drop into a bin from which it is eventually transported to an appropriate landfill. From the instant the sorbent is mixed with the gas and eventually removed from the baghouse, the sorbent reacts with the SO_2 molecules to pull them out of the gas exhaust stream. The exhaust stream that is pulled through the modules is routed out the exhaust stacks (5). On average, 70% of the SO_2 that was originally generated in the acid gas stream is emitted into the atmosphere from the calcining operation. The current dry sorbent control system reduces SO_2 emissions from K-1 by 20% while SO_2 emissions are reduced from K-2 by 40%.

Figure 3: Carbon Plant Illustration



C. Controlling SO_2 Acid Gas Emissions

The gaseous emissions generated from coke calcining operations are typically minimized by using one of three types of scrubbing control systems: wet scrubbers, semi-dry scrubbers or dry scrubbers. A dry scrubber, also called dry sorbent injection is the technology currently used at the Carbon Plan. Wet and semi-dry scrubbing systems can better handle acid gas waste streams with higher concentrations and higher volumes than dry scrubbing systems while achieving greater emission reductions; however, they cost considerably more to purchase, to install and to operate than dry scrubbing systems.

Wet Scrubbing Systems

Wet scrubbing systems are designed to capture either particulate matter or gaseous pollutants. Wet scrubbers that collect gaseous pollutants are commonly referred to as *absorbers*. In such a system, flue gas is ducted from the combustion source to an absorber vessel that injects an aqueous slurry of sorbent material into an acid-gas stream. Lime and limestone are examples of alkaline sorbents used to remove SO_2 from acid-gas streams in a wet-scrubbing process. An alkaline material is a substance that has a pH greater than 7 and is capable of neutralizing an acid. To provide optimal contact between the waste gas and the sorbent, the injection nozzles and their locations within the scrubber are designed to optimize the size and density of slurry droplets formed by the system. Optimal gas-to-liquid contact is essential to obtain high removal efficiencies in absorbers. During the reaction between the SO_2 and the sorbent material, a portion of the water in the slurry is evaporated and the waste gas stream becomes saturated with water vapor. Sulfur dioxide dissolves into the slurry droplets where it reacts with the alkaline particulates. The slurry falls to the bottom of the absorber where it is collected. Treated flue gas passes through a mist eliminator before exiting the absorber which removes any entrained slurry droplets. The absorber effluent is sent to a reaction tank where the SO_2-alkali reaction is completed thus forming a neutral salt. In a regenerative type of wet scrubbing system, regenerated slurry is recycled back to the absorber. Otherwise, the spent slurry is disposed of or can be used as a by-product. Sulfur dioxide control efficiencies for wet scrubbers range from 90% to 98%.[8]

Semi-Dry Scrubbing Systems

Semi-Dry scrubbing systems (sometimes called spray dryers) are similar to wet scrubbing systems except that the flue gas stream is not saturated with moisture. The flue gas is introduced into an absorbing vessel (dryer) where the gas is contacted with a finely atomized alkaline slurry that is usually a calcium-based sorbent. The acid gas in the stream is absorbed and neutralized by the slurry droplets. The reaction forms solid salts that are removed by a particulate control device. The heat of the flue gas is used to evaporate the water droplets thus leaving a filtered flue gas to exit the absorbing vessel. Semi-dry scrubbing systems usually can achieve control efficiencies ranging from 80% to 90%.[9]

Dry Scrubbing Systems

Another technology type for reducing SO_2 emissions from combustion sources that does not generate any liquid side-streams is a dry scrubbing system. In this process, the flue gas containing SO_2 is contacted with an alkaline material to produce a dry waste product for disposal. There are three common approaches to dry scrubbing:

- Injection of an alkaline slurry in a spray dryer with collection of dry particles in a baghouse or electrostatic precipitator (ESP);
- Dry injection of an alkaline material into the flue-gas stream with collection of dry particles in a baghouse; or,
- Addition of alkaline material to the fuel prior to or during combustion.

Dry sorbent injection (DSI) is the particular type of dry scrubbing technology currently in use at the Carbon Plant. The facility injects sodium bicarbonate sorbent material into the flue acid-gas stream after exiting a heat recovery system. The SO_2/sodium bicarbonate mixture is then filtered from the acid-gas stream via a control device called a fabric filter or baghouse. Although the Carbon Plant's SO_2 controls currently reduce emissions less than 50%, dry sorbent injection systems may achieve control efficiencies ranging usually from 50% to 60% and up to 80% emission reductions for state-of-the-art systems.[10, 11]

Baghouse Operation

As mentioned above, baghouses are a key component of dry scrubbing systems. A baghouse is an air pollution control device that removes particulates from an air or gas stream emitted from commercial processes or from combustion sources. Power plants, steel mills, pharmaceutical producers, food manufacturers, chemical producers and other industrial companies often use baghouses to control emissions of air pollutants.[12]

A baghouse consists of one or more isolated compartments containing rows of long, cylindrical bags (or tubes) made of woven or felted fabric that filter particulates. As the particle laden air or gas enters a baghouse, it is directed into a compartment containing the bags and typically travels along the surface of the bags and ultimately through the fabric. Particles are retained on the face of the bags while the filtered air stream is drawn through the bags and then vented to the atmosphere. The baghouse is operated cyclically, alternating between relatively long periods of filtering and short periods of cleaning. During cleaning, particles that have accumulated on the surface of the bags are removed and deposited in a hopper for subsequent disposal.

Baghouses are very efficient particulate collectors because of the dust cake formed on the surface of the bags. When used in tandem with other control technology, such as a dry sorbent injection system, a baghouse can affect additional emission reduction benefits. In the case of the Carbon Plant, unreacted sodium bicarbonate caked on the bag provides another opportunity for capture and neutralization of the SO_2. The Carbon Plant uses a pulse-jet type of baghouse. Figure 4 is a cut-away image of a pulse-jet baghouse.

Figure 4: Pulse-Jet Baghouse

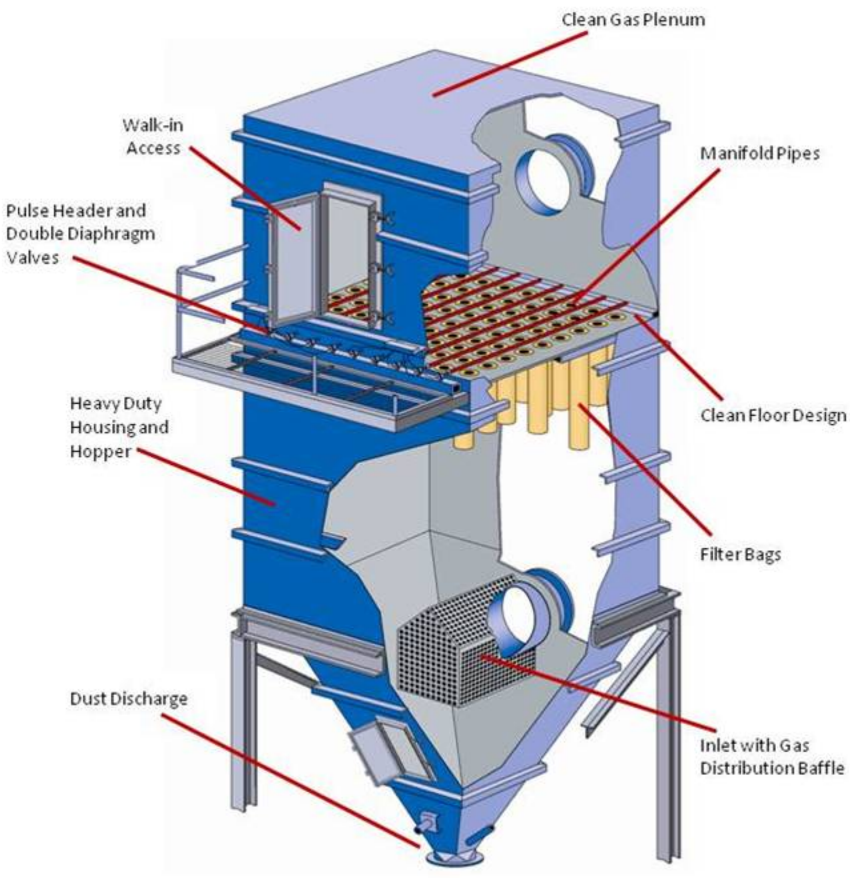


Image Source: http://www.industricorp.com/wp-content/uploads/2013/05/Jet-III-cut-a-way.jpg

IV. DRAFT RULE

Staff has reviewed the two petroleum coke calcining rules that exist in the state – South Coast Air Quality Management District (SCAQMD) Rule 1119 and San Luis Obispo Air Pollution Control District Rule 440. Both rules require an 80% SO_2 emission reduction from petroleum coke calcining operations. The petroleum coke calcining plant in San Luis Obispo County is no longer in operation, but that rule's emissions limits are still in effect. The South Coast calcining facility is subject to an 80% emission reduction requirement for SO_2. The facility's control system, a semi-dry scrubber combined with a wet electrostatic precipitator, consistently reduces SO_2 emissions in excess of 95% to comply with Rule 1119 requirements.[13]

Air District staff has worked with Carbon Plant representatives and other interested parties to find a method of achieving emission reductions that are effective, practical and cost effective. Based on lab test results, conversations with vendors and conversations with Carbon Plant representatives, Air District staff has concluded that the chemical reaction in the existing DSI system is not as efficient as it can be. The DSI system does not appear to be reducing SO_2 emissions to the maximum extent possible. The specific reasons are not yet known. The facility will have to determine if upgrading the current DSI system can meet the draft rule SO_2 emission reduction requirement or if they must use a different SO_2 control technology to meet the emission limit.

<u>Emission Standard</u>

The only other petroleum coke calcining plant currently operating in the State of California has the ability to meet an 80% SO_2 emission reduction requirement. The Air District proposes an emission limit that is equivalent to that standard. It is a mass emission standard that will limit SO_2 emissions from each Carbon Plant kiln to 50 pounds per hour (lb/hr). This mass emission limit was derived from the facility's historical continuous emission monitoring data that demonstrates when the facility operates at full capacity, uncontrolled SO_2 emissions are approximately 250 lbs/hr. A 50 lb/hr emission limit represents an 80% emission reduction.

<u>Emissions Reductions</u>

In 2010, Control Measure SSM-8 estimated potential SO_2 emission reductions of 3.6 TPD. This estimate assumed a lesser SO_2 emission abatement efficiency than is actually the case. The Air District's 2012 emissions inventory indicates the total SO_2 emissions from the calcining operation to be 3.4 TPD. This number takes into account SO_2 emission reductions currently achieved. Until recently, SO_2 abatement efficiency data was not required. Source tests had never been performed to determine SO_2 concentrations prior to acid-gas treatment. Without this number, the abatement efficiency of the DSI system was unknown. Based on new testing data by Air District staff and information provided by the Carbon Plant, the SO_2 emission reductions from the calcining operation are better understood. The DSI system reduces approximately 20% of the SO_2 emissions from K-1 and approximately 40% of the SO_2 emissions at K-2. When Regulation 9, Rule 14 is implemented, SO_2 emissions are expected to reduce by approximately 2.45 TPD. The Air District will continue to refine its estimate of emission reductions during the rule development process.

Costs

The facility's current DSI system does not meet the performance levels typically seen in such systems. It's not clear exactly what changes will be required to improve the performance of the system. It's possible that the current DSI system, once upgraded, could meet the proposed emission limit of 50 lb/hr of SO_2. This would be the least expensive solution. Staff estimates that the capital costs of upgrading the current system would range between $450,000 to $1.5 million dollars with an additional $250,000 in annual operating costs.[14]

If modest upgrades to the current system were not sufficient to meet the proposed emission limit, the facility could decide to replace the existing DSI system and install a new one. Staff anticipates that the capital costs for the purchase and installation of new DSI equipment would range between $4 million to $5 million in capital with additional $1 million to $1.5 million in annual operating costs.[15] The facility would need to conduct engineering studies and consult with vendors to determine if a new DSI system would be certain to meet the proposed emission limit.

Based on our research, Air District staff is confident that a semi-dry scrubbing system would meet the proposed 50 lb/hr emission limit. This would be the more costly than the new DSI system, but would be less expensive than the wet scrubbing system used at the coke calciner in the SCAQMD jurisdiction. Staff anticipates the capital costs to purchase and install semi-dry scrubbing equipment will range between $7 million to $10 million in capital with additional $3 million to $5 million in annual operating costs.[16]

Cost Effectiveness

To determine cost effectiveness, staff estimates the total direct and indirect cost of the installation of the equipment and then converts that to an estimated annual cost presuming a 20-year life span of the equipment. That annualized installation cost is then added to the annual operating cost to estimate a total annual cost for the emission controls. The total annual cost is then divided by the estimated annual reduction in emissions. This calculation produces a cost effectiveness estimate in terms of dollars per ton of emissions reduced.

The installation and operating costs for the various SO_2 control options described in the preceding section were derived from conversations with different vendors specializing in the design and sales of SO_2 control equipment.

Calculating the estimated emission reduction for each listed control option is not possible at this time. Site-specific engineering and testing would be required to determine the maximum emission reductions that could be achieved by upgrading the existing system.

Therefore, Air District staff cannot provide an emission reduction estimate or estimated cost effectiveness for upgrades to the DSI system.

However, based on our technical analysis, staff is confident that the facility can meet the proposed emission limit by using semi-dry scrubbing. Therefore, we can assume that a semi-dry scrubbing system would reduce emissions of SO_2 by 2.45 tpd or 890 tons per year. Assuming the high end of the installation costs ($10 million) and the high end of the annual cost estimate ($5 million per year), staff estimates the cost effectiveness to be approximately $8,700 per year.

V. RULE DEVELOPMENT / PUBLIC CONSULTATION PROCESS

In developing a draft of Regulation 9, Rule 14: Petroleum Coke Calcining Operations, Air District staff has conducted extensive research on the topic of petroleum coke calcining emissions, communicated with multiple vendors specializing in SO_2 control equipment, toured the Carbon Plant multiple times, met with Carbon Plant representatives multiple times and has had ongoing communications with the Phillips 66 Carbon Plant staff. The Air District has also conducted source tests to confirm the facility's current SO_2 emission reduction rates.

Staff also consulted with representatives from other air districts, manufacturers and suppliers of SO_2 emission control devices, and suppliers of dry sorbent material used specifically for SO_2 emission controls.

The Air District will conduct a public workshop to solicit comments from the public on draft Regulation 9, Rule 14. During the workshop, Air District staff will seek comments and answer questions on material presented in this report. Staff will review and consider all comments received during the public workshop and revise the proposal as appropriate.

Staff is specifically seeking comment on the feasibility of the draft rule from the affected facility and other interested parties. Finally, staff seeks further information on costs to modify and improve SO_2 controls currently in use at the Carbon Plant as well as the costs to purchase and install alternative SO_2 emission control technology if the facility deems it necessary to meet the draft requirement.

Staff will prepare an analysis of environmental impacts under the California Environmental Quality Act (CEQA), a socioeconomic analysis, a final draft rule and staff report that will be available for public comment prior to a public hearing before the Air District's Board of Directors.

VI. REFERENCES

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[16] Multiple consultations with SO_2 control equipment vendors Babcock & Wilcox, and, Envitech, December 2012.