

**SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT  
PLANNING, RULE DEVELOPMENT & AREA SOURCES**

**Draft Staff Report  
SO<sub>x</sub> RECLAIM  
Part I**

**Allocations, Emissions & Control Technologies**

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## Executive Summary

Part I of the ~~Preliminary~~ Draft Staff Report includes a background and a discussion on allocations, emissions, and control technologies for SO<sub>x</sub> at RECLAIM facilities. Part II ~~has not been completed and will~~ includes a discussion on appropriate BARCT levels, emission reductions, and cost effectiveness for RECLAIM facilities recommended by the consultants. Part III includes scenario analyses, RTC reductions estimates, and staff's proposal.

### ***Best Available Retrofit Control Technology under RECLAIM Program***

On October 15, 1993, the District's Governing Board adopted Regulation XX - Regional Clean Air Incentives Market (RECLAIM) and established a declining cap and trade mechanism to reduce NO<sub>x</sub> and SO<sub>x</sub> emissions from the largest stationary sources in the South Coast Air Basin (Basin). Regulation XX is comprised of 11 rules that specify the applicability, NO<sub>x</sub> and SO<sub>x</sub> facility allocations, general requirements, as well as monitoring, reporting, and recordkeeping requirements for NO<sub>x</sub> and SO<sub>x</sub> sources located at RECLAIM facilities. The RECLAIM program started with 41 SO<sub>x</sub> facilities and 392 NO<sub>x</sub> facilities. By the end of 2005 compliance year, the program included 33 SO<sub>x</sub> facilities and 304 NO<sub>x</sub> facilities.

Under the SO<sub>x</sub> RECLAIM program, the RECLAIM facilities are issued SO<sub>x</sub> annual allocations (also known as facility caps), which decline annually from 1993 until 2003 and remain constant after 2003. The annual allocations issued to the RECLAIM facilities reflect the levels of BARCT envisioned to be in place at the RECLAIM facilities, and were the results of a Best Available Retrofit Control Technology (BARCT) analysis conducted in 1993. Since 1993, the District conducted a BARCT reassessment for NO<sub>x</sub> in 2005, and has not yet conducted a BARCT reassessment for SO<sub>x</sub>. A BARCT reassessment is required by the Clean Air Act and is needed to capture the advancement in control technology and to assure that the RECLAIM facilities would achieve emission reductions as expeditiously as possible. Under the RECLAIM program, the facilities have the flexibility to either install air pollution control equipment, change method of operations, or purchase RECLAIM Trading Credits (RTCs) to meet the BARCT levels.

### ***PM<sub>2.5</sub> Implementation Rule***

In March 2007, the U.S. Environmental Protection Agency (EPA) issued a final rule, known as the *Clean Air Fine Particle Implementation Rule*, which requires non-attainment areas such as the South Coast Air Basin to meet the fine particulate (PM<sub>2.5</sub>) standards by 2010. The *Clean Air Fine Particle Implementation Rule* requires the District to achieve the fine particulate standards as expeditiously as possible, and allows the District a one time extension up to five years but no later than 2015. The rule requires the District to evaluate and employ all control measures to reduce the direct PM<sub>2.5</sub> emissions, as well as the emissions from PM<sub>2.5</sub> precursors, specifically sulfur dioxide (SO<sub>2</sub>).

### ***2007 Control Measure CMB-02 - Further SOx Reduction for RECLAIM (SOx)***

To establish the basis for future compliance with the final U.S. EPA rule, staff has developed the 2007 Air Quality Management Plan (AQMP) Control Measure CMB-02 – Further SOx Reduction for RECLAIM (SOx) adopted by the Governing Board in July 2007. This control measure proposed to further reduce SOx allocations by approximately 3 tons per day in 2011-2014 to help the basin achieve the PM2.5 standards by 2014 and indicated that that staff may need to incorporate the concept of facility modernization as described under Control Measure MCS-01 - Facility Modernization to achieve additional reductions beyond 2014.

### ***Proposed BARCT and Emission Reductions***

In 1993, the District issued a total of 12 tons per day allocation caps for the 2003 compliance year and beyond for the facilities in SOx RECLAIM. This is also the 2002 baseline for RECLAIM facilities used in the 2007 Air Quality Management Plan. In 2005, the SOx RECLAIM facilities reported a total of 10 tons per day emissions. However, 95% of the emissions was generated by the top 12 facilities; and in these 12 facilities, the top 7 source categories listed below were responsible for ~~90~~80% of the facility emissions.

- Fluid catalytic cracking units;
- Boilers and heaters using refinery gas;
- Sulfur recovery and tail gas treatment units;
- Sulfuric acid manufacturing plants;
- Container glass melting furnace;
- Coke calciner;
- Cement kilns and a coal steam boiler at a cement manufacturing facility.

These top emitters emitted approximately 7.53 tons per day in 2005. They were issued an overall allocation of approximately 9.82 tons per day for the 2000 compliance year, and 6.41 tons per day for the 2003 compliance year (34.75% shave) as shown in Table EX-1.

**TABLE EX-1**  
**Allocations and Emissions for Top Seven Category of Sources**

Process	Allocations		Emissions	
	Yr 2000 (tpd)	Yr 2003 (tpd)	Yr 2005 (tpd)	Reduction (tpd)
FCCUs	2.17	1.42	3.55	TBD
Boilers/Heaters	0.89 <sup>(1)</sup>	0.58 <sup>(1)</sup>	0.91 <sup>(2)</sup>	TBD
Sulfur Recovery & Tail Gas Treatment	1.61	1.05	0.96	TBD
Sulfuric Acid Manufacturing	2.53	1.65	1.16	TBD
Container Glass Manufacturing	1.01	0.66	0.32	TBD
Coke Calciner	1.28	0.84	0.35	TBD
Portland Cement Manufacturing	0.33	0.22	0.27	TBD
<b>Total</b>	<b>9.82</b>	<b>6.41</b>	<b>7.53</b>	<b>TBD</b>

Note: 1) For all boilers and heaters at refineries. 2) For the top 17 emitters at refineries.

Staff has conducted a detailed research on control technologies for these 7 top sources of SO<sub>x</sub> emissions as discussed in Chapter 3 – Chapter 9, and summarized in Table EX-2.

**TABLE EX-2**  
**Proposed Control Technology**

Process	Control Technology
FCCU	<ol style="list-style-type: none"> <li>1. Hydrotreating</li> <li>2. SO<sub>x</sub> reducing catalysts (e.g. Intercat, Grace Davidson)</li> <li>3. Wet gas scrubbers (e.g. BELCO scrubber, Cansolv regenerative scrubber)</li> <li>4. Combination of the above</li> </ol>
Boilers Heaters	<ol style="list-style-type: none"> <li>1. Fuel Gas Treating</li> <li>2. Wet gas scrubbers (e.g. BELCO scrubber, Cansolv regenerative scrubber)</li> <li>3. Combination of the above</li> </ol>
Sulfur Recovery & Tail Gas Treatment	<ol style="list-style-type: none"> <li>1. Increase efficiency of sulfur recovery (e.g. using catalysts such as SELECTOX, or adding three or more converters to the Claus unit)</li> <li>2. Increase efficiency of tail gas treatment unit (e.g. using more efficient absorbents or catalysts)</li> <li>3. Wet gas scrubbers (e.g. DynaWave scrubber, Cansolv regenerative scrubber)</li> <li>4. Combination of the above</li> </ol>
Sulfuric Acid Manufacturing	<ol style="list-style-type: none"> <li>1. Upgrading converters and absorbers,</li> <li>2. Using cesium promoted vanadium catalysts,</li> <li>3. Wet gas scrubbers (e.g. Cansolv scrubber)</li> <li>4. Combination of the above</li> </ol>
Container Glass Manufacturing	Wet scrubber (e.g. Tri-Mer Cloud Chamber scrubber)
Coke Calciner	<ol style="list-style-type: none"> <li>1. Dry scrubber; or</li> <li>2. Wet scrubber and wet ESP</li> </ol>
Portland Cement Manufacturing	Dry or Wet scrubber

The control technologies proposed in Table EX-2 would be employed to generate at least 3 tpd emission reductions for SO<sub>x</sub> RECLAIM, which will be addressed in Part II of a subsequent update to this Preliminary Draft Staff Report.

## Chapter 1 - Background

### 1.1 Legislative Authority

The California Legislature created the Air Quality Management District (AQMD) in 1977 (the Lewis-Presley Air Quality Management Act, Health and Safety Code Section 40400 et seq.) as the agency responsible for developing and enforcing air pollution control rules and regulations in the South Coast Air Basin (Basin). By statute, the AQMD is required to adopt an Air Quality Management Plan (AQMP) demonstrating compliance with all state and federal ambient air quality standards for the Basin (Health and Safety Code (H&SC) §40460(a)). In addition, the AQMD must adopt rules and regulations that implement the AQMP (H&SC §40440(a)).

The California Clean Air Act (CCAA) also requires the AQMD to achieve and maintain state standards by the earliest practicable date and for extreme non-attainment areas and to implement all Best Available Retrofit Control Technologies (BARCT) for existing sources. H&SC §40406 specifically defines BARCT as “...best available retrofit technology means an emission limitation that is based on the maximum degree of reduction achievable taking into account environmental, energy, and economic impacts by each class or category of source.”

### 1.2 Fine Particle Regulation and SO<sub>x</sub> Control

Scientific studies have found an association between exposure to particulate matter and significant health problems, including: aggravated asthma; chronic bronchitis; reduced lung function; irregular heartbeat; heart attack; and premature death in people with heart or lung disease. Individuals particularly sensitive to fine particle exposure include older adults, people with heart and lung disease, and children.

In July 1997, the U.S. EPA promulgated the National Ambient Air Quality Standards for Fine Particles (PM-2.5). The annual standard is a level of 15 micrograms per cubic meter ( $\mu\text{g}/\text{m}^3$ ) based on a 3-year average of annual mean PM<sub>2.5</sub> concentrations. The 24-hour standard is a level of 65  $\mu\text{g}/\text{m}^3$ , based on a 3-year average of the 98th percentile of 24-hour concentrations. In September 2006, EPA significantly strengthened the previous daily fine particle standard from 65  $\mu\text{g}/\text{m}^3$  to 35  $\mu\text{g}/\text{m}^3$ . This standard increases protection of the public from short-term exposure to fine particles.

There are multiple areas across the country exceeding the federal PM<sub>2.5</sub> standards. Unfortunately, Southern Californians are burdened with a disproportional share of the PM<sub>2.5</sub> exposure estimated to be 52 percent of the nation wide exposure resulting in approximately 5,400 premature death annually.

In March 2007, EPA issued a final rule, known as the *Clean Air Fine Particle Implementation Rule*, requires non-attainment areas to meet PM 2.5 standards by 2010. The Basin is classified as a non-attainment area and the District must develop an Air Quality Management Plan by 2008 to address the implementation processes to substantially reduce PM2.5 in order to meet the PM2.5 standards by 2010. The attainment date of 2010 may be extended for up to five years, however the District must achieve PM2.5 standards as expeditiously as possible, no later than 2015. The recently adopted AQMP revision in 2007 serves as the region's attainment demonstration to the federal ozone and PM2.5 standards and includes a formal request to the U.S. EPA to extend the PM2.5 attainment date to 2015.

Five main types of pollutants contribute to ambient PM2.5 concentrations: direct PM2.5 emissions, sulfur dioxide, nitrogen oxides, ammonia and volatile organic compounds. The effect of reducing emissions of each of these pollutants varies by areas depending on the composition, concentrations of these pollutants and other area-specific factors. The EPA's *Clean Air Fine Particle Implementation Rule* requires the District to implement all reasonably available control measures (RACM) and reasonably available control technology (RACT), considering economic and technical feasibility and other factors, that are needed to show that the area will attain the fine particle standards as expeditiously as practicable. In this *Clean Air Fine Particle Implementation Rule*, the U.S. EPA specifically requires the non-attainment areas to evaluate all control measures to reduce direct PM2.5 emissions, as well as PM2.5 precursors, especially SOx. While the 2007 AQMP lays out a multi-pollutant control strategy to demonstrate attainment with the federal PM2.5 standards, it identifies NOx and SOx reductions by far as the two most effective tools in reaching attainment with the PM2.5 standards.

### 1.3 Current RECLAIM Program

On October 15, 1993, the District's Governing Board adopted the RECLAIM program and Regulation XX. Regulation XX includes 11 rules that specify the applicability, NOx and SOx allocations, general requirements, as well as monitoring, reporting, and recordkeeping requirements. The RECLAIM program started with 41 SOx and 392 NOx facilities in 1993. By the end of 2005 compliance year, the program includes 33 SOx and 304 NOx facilities.

Under the RECLAIM program, facilities are issued SOx and NOx annual allocations, or also known as facility caps. The facility caps declined annually to reflect the levels of BARCT that were envisioned to be in place at the RECLAIM facilities. To meet the annual declining allocation, RECLAIM facilities have the flexibility of installing pollution control equipment, changing operations, or purchasing RECLAIM Trading Credits (RTCs). It was envisioned that a BARCT analysis be conducted every three years to capture ~~the~~any advancement in control technology and to assure that the RECLAIM program would achieve emission reductions as expeditiously as possible.

Throughout the years, there have been a number of amendments to the RECLAIM rules. In January 2005, a BARCT analysis was re-conducted for NOx, and as a result of this analysis, the



RECLAIM rules were amended and the NO<sub>x</sub> annual allocations previously given to the NO<sub>x</sub> RECLAIM facility were further reduced by approximately 20% to reflect BARCT.

For SO<sub>x</sub>, the annual allocations given decline annually from 1993 until 2003, and remain constant since 2003. The 2003 SO<sub>x</sub> allocations reflected the BARCT levels envisioned for SO<sub>x</sub> in 1993. BARCT analysis for SO<sub>x</sub> has not been reevaluated since 1993, and is reevaluated with this proposed amendment.

## 1.4 Control Measure CMB-02

Control Measure CMB-02 estimated that BARCT would be implemented to achieve approximately 3 tons per day SO<sub>x</sub> emission reductions from 2011 to 2014. The control measure estimated that reducing sulfur content in refinery fuel gas could achieve approximately 1.6 tons per day SO<sub>x</sub>; and reducing SO<sub>x</sub> emissions from fluid catalytic cracking units could achieve 1.3 tons per day SO<sub>x</sub>. It was expected that the control measure implementation may either affect all SO<sub>x</sub> RECLAIM facilities or only affect the facilities that have highest SO<sub>x</sub> emissions and that can employ BARCT. During the rulemaking process, it was envisioned that staff will also explore the feasibility to incorporate the control concept of Control Measure MCS-01 - Facility Modernization to achieve reductions beyond 2014.

## 1.5 Affected Facilities

Currently, there are 33 facilities in the SO<sub>x</sub> RECLAIM Program. These facilities have SO<sub>x</sub> emissions greater than or equal to four tons per year in 1990 or any subsequent year. SO<sub>x</sub> facilities in the RECLAIM program have a wide range of equipment such as Fluidized Catalytic Cracking Units (FCCU), furnaces, kilns, sulfuric acid plants, tail gas units, boilers, heaters, internal combustion engines, and gas turbines. The emission inventory of these facilities and the top emitters at these facilities is discussed in Chapter 2.

## 1.6 Outline of the ~~Preliminary~~ Draft Staff Report, Part I

The primary purpose of this amendment is to reduce the SO<sub>x</sub> RECLAIM allocations to reflect the current levels of BARCT. Staff conducted an extensive research on control technologies for the following 7 top emitting source categories of equipment:

- Fluid catalytic cracking units at refineries;
- Boilers and heaters using refinery fuel at refineries;
- Sulfur recovery and tail gas treatment units at refineries;
- Furnace for sulfuric acid manufacturing plants;
- Glass melting furnace at a container glass manufacturing plant;
- Coke calciner at a coke calcining facility; and
- Cement kilns and a coal steam boiler at a Portland cement manufacturing facility.

The potential control technologies for the above 7 categories of equipment are presented in Chapter 3 to Chapter 9. In each Chapter, staff provides and discusses the following information in Part I of the ~~Preliminary~~ Draft Staff Report:

- A brief description of the process that generates SO<sub>x</sub>;
- Current allocations issued for each source;
- The 2005, 2006 and 2007 SO<sub>x</sub> emissions reported for each source;
- The applicable SO<sub>x</sub> control technologies for each source; and
- If available, the costs and cost effectiveness reported in literature for each applicable control

The analyses in Chapter 3 – Chapter 9 reflect the control technologies that have been used at various facilities in the U.S. and that are determined to be cost-effective for these facilities. With the implementation of these technologies, an overall reduction of at least 3 tons per day is expected and could be achieved from 2011 – 2014 as proposed in 2007 Control Measure CMB-02.

In Part II of the ~~Preliminary~~ Draft Staff Report, staff will address the appropriate BARCT level for each source category, the potential emission reductions, and cost effectiveness. As new information surfaces, staff will update Chapter 2 – Chapter 9 accordingly. Staff will also develop other chapters ~~Chapter 10 – Chapter 12~~ in the near future. ~~Chapter 10 will include cost analyses for several scenarios that could result in a reduction of 3 tons per day SO<sub>x</sub>. Chapter 11 will include a description of the proposed rule amendments and Chapter 12 will provide a summary of the impact assessment (e.g. CEQA and socioeconomic analysis).~~

## Chapter 2 - Emission Inventory

### 2.1 2007 Air Quality Management Plan

The 2007 Air Quality Management Plan (AQMP) was based on the 2002 base year inventory. In the 2007 AQMP, RECLAIM facilities were reported to emit a total of 12 tons per day SO<sub>x</sub> as shown in Table 2-1. The SO<sub>x</sub> emissions from RECLAIM represented more than 50% of the total SO<sub>x</sub> emissions from stationary sources, and 23% of the total SO<sub>x</sub> emissions from the entire basin.

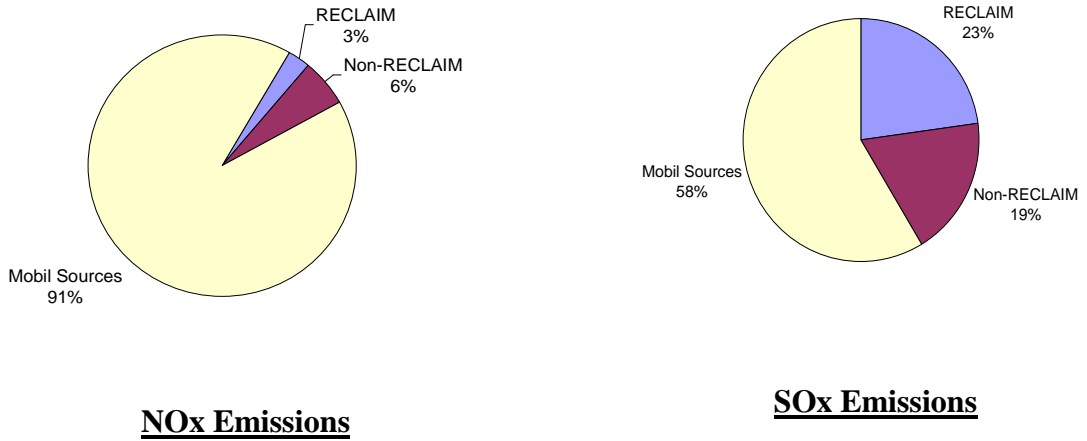
**TABLE 2-1**  
**Summary of Emissions By Major Source Category (2002 Base Year)**  
**(Tons per Day)**

Source Category	NO <sub>x</sub>	SO <sub>x</sub>
Stationary Sources		
Fuel Combustion	35	2
Waste Disposal	2	0
Cleaning and Surface Coatings	0	0
Petroleum Production and Marketing	0	7
Industrial Processes	0	0
Solvent Evaporation		
Consumer Products	0	0
Architectural Coatings	0	0
Others	0	0
Misc. Processes	27	0
<b>RECLAIM Sources</b>	<b>29</b>	<b>12</b>
<b>Total Stationary Sources</b>	<b>93</b>	<b>22</b>
<b>Total Mobile Sources</b>	<b>1000</b>	<b>31</b>
<b>TOTAL</b>	<b>1093</b>	<b>53</b>

Reference: 2007 AQMP. The actual emissions from RECLAIM facilities of 12 tpd were also reported in the “Annual RECLAIM Audit Report for the 2002 Compliance Year”, dated March 5, 2004. Total RTCs (allocations and converted ERCs) were reported to be 13 tpd in the 2002 RECLAIM Audit Report.

Data presented in Table 2-1 and Figure 2-1 present a sharp distinction between the distribution of NO<sub>x</sub> versus SO<sub>x</sub> emissions in the basin, and explain the importance of undertaking a BARCT reassessment for RECLAIM facilities in this amendment of Regulation XX. As shown in Table 2-1 and Figure 2-1, the RECLAIM facilities generated only about 3% of NO<sub>x</sub> emissions in the entire South Coast Air Basin (Basin). A majority of NO<sub>x</sub> emissions in the Basin comes from mobile sources. In contrast, the RECLAIM facilities generated a significant 23% of SO<sub>x</sub> emissions in the Basin and contributed more than 50% of SO<sub>x</sub> emissions from stationary sources.

**FIGURE 2-1  
NOx and SOx Emission Distribution (2002 Baseline)**



The top 10 ranking source of SOx emissions in the basin in 2002, 2014 and 2023 are shown in Table 2-2. SOx emissions from RECLAIM facilities are ~~significantly high since they are~~ ranked #2, second only to ships and commercial boats. Given the effectiveness of the SOx reduction in improving PM2.5 air quality and ultimately reaching the federal PM2.5 standards, searching for additional emission reductions in RECLAIM category sources becomes an important effort.

**TABLE 2-2  
Top Ten Ranking of SOx Emissions From Highest to Lowest**

	2002 Base Year	2014 Base Year	2023 Base Year
1	Ships & Commercial Boats	Ships & Commercial Boats	Ships & Commercial Boats
2	RECLAIM Sources	RECLAIM Sources	RECLAIM Sources
3	Non-RECLAIM Refineries Sources	Aircraft	Aircraft
4	Heavy-Duty Diesel Trucks	Manufact/Industrial Combustion	Manufact/Industrial Combustion
5	Aircraft	Light-Duty Passenger Cars	Light-Duty Passenger Cars
6	Trains	Light-Duty Trucks	Light-Duty Trucks
7	Off-Road Equipment	Service/Commercial Combustion	Service/Commercial Combustion
8	Light-Duty Passenger Cars	Non-RECLAIM Refineries Sources	Non-RECLAIM Refineries Sources
9	Manufact/Industrial Combustion	Waste Burning & Disposal	Waste Burning & Disposal
10	Light-Duty Trucks	Residential Fuel Combustion	Residential Fuel Combustion

Reference: 2007 AQMP. Note that Non-RECLAIM sources are sources that are not included in the RECLAIM program such SOX emissions emitted from flares or generated under upset conditions.

The 2007 AQMP calls for significant reductions of SOx from both stationary and mobile sources by 2014. As shown in Table 2-3, a regional modeling in the 2007 AQMP indicates that an overall emission reduction of 24 tons per day SOx is needed to meet the particulate standard in 2014. In that 24 tons per day reduction, mobile source control measures from California Air Resources Board and the District can potentially ~~generate~~ reduce 21 tons per day. The remaining 3 tons per day reductions comes from the one-and-only stationary source control measure for

RECLAIM facilities. A BARCT reassessment for SO<sub>x</sub> is therefore essential to identify the potential sources that can generate the 3 tons per day SO<sub>x</sub> reduction required for 2014.

**TABLE 2-3**  
**Emission Reductions for 2014 Based On**  
**Average Annual Emissions Inventory (tons per day)**

Sources	SO <sub>x</sub>
Year 2014 Baseline	43
Emission Reductions:	
• District's Short Term/Mid-Term Stationary Source Control Measures	<b>3</b>
• CARB's Proposed State Strategy	20
• District's Proposed Mobile Source Control Measures	1
Total Reductions (All Measures)	24
2014 Remaining Emissions	19

Reference: Table 4-10 of 2007 AQMP

## 2.2 2005 Annual Emissions Report

RECLAIM facilities reported a total of 10 tons per day SO<sub>x</sub> from January to December 2005. As shown in Table 2-3, the top twelve SO<sub>x</sub> emitting facilities emitted 9.47 tons per day SO<sub>x</sub>, which are about 95% of total emissions from RECLAIM universe. The top 12 emitting facilities where staff will focus in to find the sources of emission reductions include:

- Six refineries: BP, ConocoPhillips, Chevron, ExxonMobil, Ultramar, and Equilon (Equilon is now Tesoro.)
- Two sulfuric acid plants: Rhodia Inc. and ConocoPhillips
- One coke calciner plant: BP located in Wilmington
- One cement manufacturing plant: California Portland Cement Co.
- Two container glass manufacturing plants: Owens Brockway Glass Container Inc and Saint-Gobain Containers Inc which is currently shutdown.

**TABLE 2-3**  
**SO<sub>x</sub> Emissions at RECLAIM Facilities (Calendar Compliance Year 2005)**

Facility ID	Facility Name	Cycle	Emissions (tons per year)	Emissions (tons per day)	Cumulative Percentage
131003	BP WEST COAST PROD.LLC BP CARSON REFINERY	2	679.4	1.86	19%
800363	CONOCOPHILLIPS COMPANY	2	421.2	1.15	30%
114801	RHODIA INC.	1	410.7	1.13	42%
800370	EQUILON ENTER., LLC, SHELL OIL PROD. U S	1	363.6	1.00	52%
800030	CHEVRON PRODUCTS CO.	2	362.5	0.99	62%
800089	EXXONMOBIL OIL CORPORATION	1	333.5	0.91	71%
800026	ULTRAMAR INC	1	312.8	0.86	80%
800362	CONOCOPHILLIPS COMPANY	1	210.7	0.58	85%
131249	BP WEST COAST PRODUCTS LLC,BP WILMINGTON	1	130.1	0.36	89%
800181	CALIFORNIA PORTLAND CEMENT CO	2	100.5	0.28	92%
7427	OWENS-BROCKWAY GLASS CONTAINER INC	1	74.7	0.20	94%
108701	SAINT-GOBAIN CONTAINERS, INC.	1	55.9	0.15	95%
	OTHER RECLAIM FACILITIES	1 and 2	165.0	0.45	100%
<b>Total</b>			<b>3621</b>	<b>9.92</b>	

Reference: 2005 Annual Permit Emissions Report (January 2005 – December 2005)

Table 2-4 shows the distribution of SO<sub>x</sub> emissions with respect to the equipment/processes at RECLAIM facilities. As shown in Table 2-4, top emitters at RECLAIM facilities include mainly fluid catalytic cracking units, sulfur recovery and tail gas treatment units, refinery boilers and heaters burning refinery gases, coke calciner, cement kilns, sulfuric acid absorption tower and glass melting furnaces. Staff will focus in reassessing BARCT for these top emitters which emit more than 80% of SO<sub>x</sub> emissions at RECLAIM facilities.

**TABLE 2-4**  
**Distribution of SO<sub>x</sub> Emissions at RECLAIM Facilities**  
**By Equipment/Processes**

Equipment/Processes	Percentage of Emissions
Fluid Catalytic Cracking Units	33%
Sulfur Recovery & Tail Gas Units	10%
Refinery Process Heaters and Boilers	31%
Cement Kilns – Glass Melting Furnaces	7%
Sulfuric Acid Manufacturing	12%
Other Miscellaneous Processes/Equipment	7%

Reference: 2005 baseline emissions

Table 2-5 shows SO<sub>x</sub> emissions reported from 2002 to 2007, grouped by compliance year and calendar year. (As an example, SO<sub>x</sub> emissions reported for the 2003 compliance year were the emissions reported from January 1, 2003 – December 31, 2003 for Cycle 1 RECLAIM facilities, and from July 1, 2003 – June 31, 2004 for Cycle 2 facilities. SO<sub>x</sub> emissions reported for the 2003 calendar year were the emissions reported from January 1, 2003 – December 31, 2003 for both Cycle 1 and Cycle 2 facilities.)

The average reported emissions from 2003 – 2007 compliance year were approximately 10 tpd (Staff did not include year 2002, and the years before 2002 in the average, because the Tier II shave started in 2003.)

The difference (Delta 2) between the emissions for each compliance year and the average emissions from 2003-2007, and the difference (Delta 3) between the emissions for each calendar year and the average emissions from 2003-2007 were shown in Table 2-5. Comparing Delta 1 and Delta 2 for all the emissions from 2003-2007, the 2005 calendar year emissions stand out to be the most representative emissions for this 5-year period with Delta 3 less than 1%.

**TABLE 2-5**  
**SOx Emissions Reported by RECLAIM Facilities from 2002 – 2007**  
**Grouped By Compliance Year & Calendar Year**

<u>Year</u>	<u>SOx Emissions by Compliance Year</u>	<u>SOx Emissions by Calendar Year</u>	<u>Delta1</u>	<u>Delta2</u>	<u>Delta3</u>
	<u>(tpd)</u>	<u>(tpd)</u>	<u>(%)</u>	<u>(%)</u>	<u>(%)</u>
<u>2002</u>	<u>11.84</u>	<u>12.17</u>	<u>11</u>	<u>17.4</u>	<u>20.7</u>
<u>2003</u>	<u>10.56</u>	<u>11.08</u>	<u>10</u>	<u>4.8</u>	<u>9.9</u>
<u>2004</u>	<u>9.85</u>	<u>9.85</u>	<u>9</u>	<u>-2.3</u>	<u>-2.3</u>
<b><u>2005</u></b>	<b><u>9.92</u></b>	<b><u>10.13</u></b>	<b><u>9</u></b>	<b><u>-1.6</u></b>	<b><u>0.4</u></b>
<u>2006</u>	<u>9.81</u>	<u>10.24</u>	<u>9</u>	<u>-2.7</u>	<u>1.6</u>
<u>2007</u>	<u>10.27</u>			<u>1.9</u>	
<b><u>Average (2003 - 2007)</u></b>	<b><u>10.08</u></b>				

Note: 1) Reference of data i) RECLAIM Admin team, e-mail 8/2008, ii) RECLAIM Annual Audit March 2009; 2) Delta 1 is the difference between emissions grouped by compliance year and emissions grouped by calendar year; 3) Delta 2 is the difference between the average emissions from 2003-2007 and the emissions reported for each compliance year, 4) Delta 3 is the difference between the average emissions from 2003-2007 and the emissions reported for each calendar year.

## Chapter 3 - Fluid Catalytic Cracking Units

### 3.1 Process Description

There are six refineries that operate six fluid catalytic cracking units (FCCU) in the District: Chevron, BP West Coast, ExxonMobil, ConocoPhillips, Ultramar and Tesoro. The FCCUs are classified as major sources of emissions in RECLAIM, and as such, the emissions from FCCUs are required to be monitored with continuous emission monitoring system (CEMS), and reported on a daily basis electronically to the District. A brief description of the process is presented below.

The FCCU is the most important and widely used refinery process for converting heavy oils into more valuable gasoline and lighter products. The process uses a very fine catalyst that behaves as a fluid when aerated with a vapor. The fluidized catalyst is circulated continuously between a reactor and a regenerator and acts as a vehicle to transfer heat from the regenerator to the oil feed in the reactor. The cracking reaction is endothermic and the regeneration reaction is exothermic. A schematic of a fluid catalytic cracking unit (FCCU) is shown in Figure 3-1.

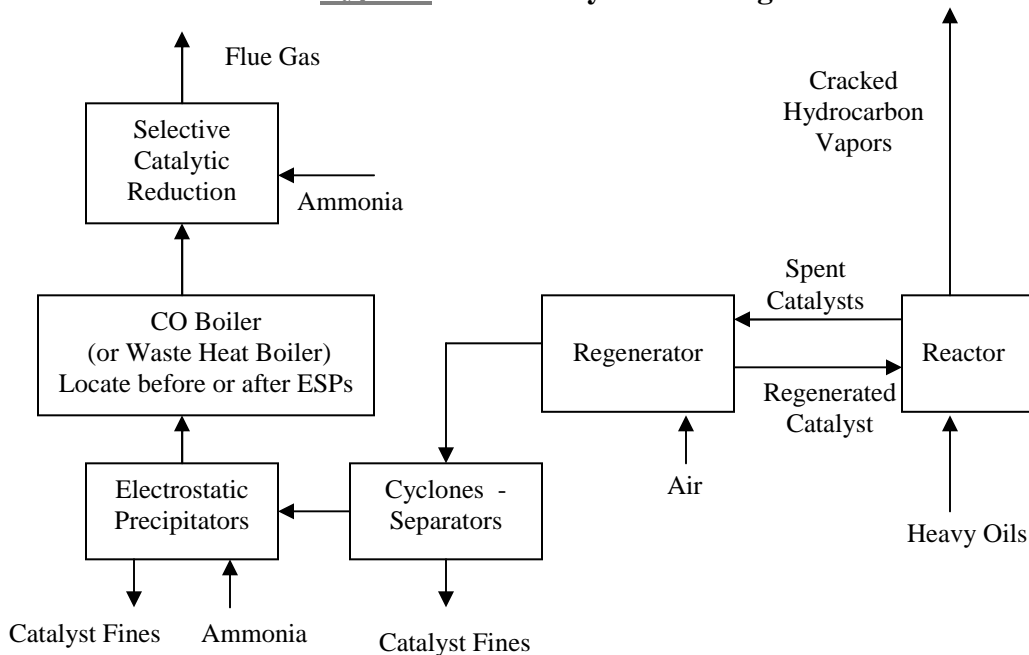
The fresh feed is preheated by heat exchangers to a temperature of 500-800 degree Fahrenheit and enters the FCCU at the base of the feed riser where it is mixed with the hot regenerated catalyst. The heat from the catalyst vaporizes the feed and brings it up to the desired reaction temperature. The mixture of catalyst and hydrocarbon vapor travels up the riser into the reactor. The cracking reaction starts in the feed riser and continues in the reactor. Average reactor temperatures are in the range of 900-1000 degree Fahrenheit. As the cracking reaction progresses, the catalyst surface is gradually coated with carbon (coke), reducing its efficiency. While the cracked hydrocarbon vapors are routed overhead to a distillation column for separation into lighter components, the oil remaining on the catalyst is removed by steam stripping before the spent catalyst is cycled to the regenerator.

In the regenerator, the coke is burned off with air and the spent catalyst is reactivated. The regenerator can be designed and operated to either partially burn the coke on the catalyst to a mixture of carbon monoxide (CO) and carbon dioxide (CO<sub>2</sub>), or completely burn the coke to CO<sub>2</sub>. The regenerator temperature is carefully controlled to prevent catalyst deactivation by overheating and to provide the desired amount of carbon burn-off. This is done by controlling the air flow to give a desired CO<sub>2</sub>/CO ratio in the exit flue gases or the desired temperature in the regenerator. The flue gas containing a high level of CO is routed to a supplemental-fuel fired CO boiler if needed to completely burn off the CO to CO<sub>2</sub>. Generally, FCCUs operate in a completely burn mode; and in this scenario, the CO boiler ~~is~~might be used as a heat ~~exchanger~~recovery device without any supplemental fuel. The regenerated catalyst is generally steam-stripped to remove adsorbed oxygen before being cycled back to the reactor. The regenerator exit temperatures for catalyst are about 1,200-1,450 degree Fahrenheit.



It is during the regeneration cycle that some of the catalyst is lost in the form of catalyst fines. The catalyst fines escape the regenerator in both the flue gas and the hydrocarbon vapor stream going to the fractionation column. The FCCU is a major source of sulfur oxides, nitrogen oxides and particulate matter in the refinery. To control particulate emissions, flue gas from the regenerator is routed through a series of cyclones and electrostatic precipitators—~~matter~~. Selective catalytic reduction is can be used to reduce nitrogen oxides emissions. The control options for sulfur oxides are discussed in Section 3.3 below.

**FIGURE 3-1**  
**Typical Fluid Catalytic Cracking Process**



## 3.2 Current Allocations and Emissions

### 3.2.1 Allocations

In 1993, the six refineries in the basin were issued emission allocations to their FCCUs based on an emission factor (also known as Tier I emission factor) of 13.7 lbs SO<sub>x</sub> per thousand barrels refinery feed. The activity of each FCCU used in the allocation determination in 1993, and the emissions allocated to each FCCU are listed in Table 3-1. The total Tier I allocations provided for the six FCCUs are 2.17 tons per day.

### 3.2.2 Emissions

Since FCCUs are classified as major sources in RECLAIM, the SO<sub>x</sub> emissions from the FCCUs are monitored with CEMS and reported on a daily basis to the District. The total annual emissions from January 2005 – December 2005 from the FCCUs is about 3.55 tons per day as shown in Table 3-2.

The FCCUs at RECLAIM facilities are not subject to any specific concentration or emission rate standards. RECLAIM facilities are given the flexibility to operate their equipment as long as the total emissions from the facility is at or below the facility emission caps. The allocations provided to the FCCUs since 1993 have not been adjusted even though there are commercially available technologies that can be used to further reduce SOx emissions from the FCCUs. In addition, the capacity of each FCCU may increase since the level reported in 1993, which warrants for a need to upgrade the capacity of the control device.

**TABLE 3-1**  
**SOx Allocations for FCCUs**

<b>Facility</b>	<b>Peak Year</b>	<b>Emission Factor (lbs/1000 barrels)</b>	<b>Tier I Allocations (lbs/year)</b>	<b>Tier I Allocations (tons/day)</b>
A	1992	13.7	297,345	0.41
B	1990	13.7	414,233	0.57
C	1988	13.7	188,545	0.26
D	1992	13.7	374,037	0.51
E	1991	13.7	127,684	0.18
F	1990	13.7	172,291	0.24
			<b>Total</b>	<b>2.17</b>

Reference: Allocation files for each facility developed based on reported data in 1993.

**TABLE 3-2**  
**Current SOx Emissions from FCCUs**

<b>Facility</b>	<b>2005 SOx Emissions (tons/day)</b>	<b>2006 SOx Emissions (tons/day)</b>	<b>2007 SOx Emissions (tons/day)</b>
A	0.39	0.36	0.33
B	1.03	0.70	0.71
C	0.96	1.00	0.97
D	0.31	0.27	0.20
E	0.25	0.28	0.18
F	0.61	0.89	0.56
	<b>3.55</b>	<b>3.50</b>	<b>2.95</b>

Note: The 2005 SOx emissions were from SCAQMD database for the period from January 2005 – December 2005. The 2006 and 2007 emissions were reported by the facilities through a Survey Questionnaire distributed by SCAQMD in 2008. The SOx outlet concentrations at 0% O2 were either data reported by the facilities through the Survey conducted in 2008, or data in the source test results provided by SCAQMD source testing team.

Based on responses from the facilities to the 2008 SCAQMD Survey Questionnaire, staff estimated that the six refineries were operated at the current emission rates listed in Table 3-3.

**TABLE 3-23**  
**Current SOx Emission Rates & Concentrations from FCCUs**

<b>SOx Outlet Concentrations (ppmv)</b>	<b>Emission Rate (lbs/1000 barrels feed)</b>
Average 18 ppmv	10.99
Average 36 ppmv	21.68
35 ppmv – 95 ppmv	34.91
Average 12 ppmv	6.89
Average 11 ppmv	16.67
Average 58 ppmv	22.18
<b>Average of 6 Refineries</b>	<b>17.93</b>

### 3.3 Control Technology

The potential available control technologies to reduce SOx emissions from a FCCU are:

1. Processing of low sulfur feed stocks,
2. Feed hydro-treating,
3. Flue gas scrubbing,
4. Using SOx reducing additives,
5. Using combination of the above control technologies

Currently, the six refineries in the Basin have processed low sulfur feed stocks and use feed hydrotreating. Five refineries in the District have experimented with SOx reducing additives, and one refinery has chosen to install a wet scrubber to reduce SOx and PM concurrently. Table 3-34 provides a list of control technologies that are currently used at various refineries in the United States to achieve a SOx outlet emission level of 25 ppmvd at 0% O<sub>2</sub>, 365-day rolling average, and 50 ppmvd at 0% O<sub>2</sub>, 7-day rolling average. ~~These levels are lower than the levels emitted from several FCCUs in the District.~~ To achieve these emission levels, the refineries in the U.S. typically use wet scrubbers or SOx reducing catalysts.

**TABLE 3-34**  
**SOx Control Technology for FCCU**

<b>Refinery</b>	<b>SOx Limit</b>	<b>Technology</b>	<b>Implementation</b>
Marathon Petroleum Co LLC., Garyville Refinery, Louisiana <sup>(1)</sup>	25 ppmvd at 0% O <sub>2</sub> , 365-day rolling average	Wet Gas Scrubber	NA
Sunoco Philadelphia FCCU w CO boiler <sup>(2)</sup>	25 ppmvd at 0% O <sub>2</sub> , 365-day rolling average; 50 ppmvd at 0% O <sub>2</sub> , 7-day rolling average.	Wet Gas Scrubber	June 2008
BP, Texas City, Texas <sup>(4)</sup>	25 ppmvd at 0% O <sub>2</sub> , 365-day rolling average	Wet Gas Scrubber & SOx Reducing Catalysts	2006

**TABLE 3-34 (Continued)**  
**SOx Control Technology for FCCU**

<b>Refinery</b>	<b>SOx Limit</b>	<b>Technology</b>	<b>Implementation</b>
Valero Delaware City, FCCU w CO boiler <sup>(2), (5)</sup>	25 ppmvd at 0% O <sub>2</sub> , 365-day rolling average; 50 ppmvd at 0% O <sub>2</sub> , 7-day rolling average; 361 tons/year. <u>The system is in operation since 2006, and has continuously achieved 1 ppmv – 2ppmv SO<sub>x</sub>, 0% O<sub>2</sub>.</u>	Regenerative Wet Gas Scrubber System including a BELCO pre-scrubber, an amine-based regenerative CANSOLV packed-bed absorber, and a caustic polisher.	By 2006
Sumoco Eagle Point, FCCU <sup>(2)</sup>	25 ppmvd at 0% O <sub>2</sub> , 365-day rolling average; 50 ppmvd at 0% O <sub>2</sub> , 7-day rolling average.; 67.4 lbs/hr on 1-hr block average.	Wet Gas Scrubber	By 2008
ConocoPhillips Bayway, FCCU w two CO boilers. <sup>(2)</sup>	25 ppmvd at 0% O <sub>2</sub> , 365-day rolling average; 50 ppmvd at 0% O <sub>2</sub> , 7-day rolling average.	Wet Gas Scrubber	By 2005
ConocoPhillips Trainer, FCCU w two CO boilers. <sup>(2)</sup>	25 ppmvd at 0% O <sub>2</sub> , 365-day rolling average; 50 ppmvd at 0% O <sub>2</sub> , 7-day rolling average.	Wet Gas Scrubber	By 2006
<del>Motiva, Delaware City, DE <sup>(2)</sup></del>	<del>25 ppmvd at 0% O<sub>2</sub>, 365-day rolling average (152,000 barrels per day capacity FCCU)</del>	<del>Wet Gas Scrubber</del>	<del>2003–2005</del>
Motiva, Convent, LA <sup>(2)</sup>	25 ppmvd at 0% O <sub>2</sub> , 365-day rolling average (225,000 barrels per day capacity FCCU)	Wet Gas Scrubber	2006 – 2007
Motiva, Port Arthur, TX <sup>(3)</sup>	25 ppmvd at 0% O <sub>2</sub> , 365-day rolling average (235,000 barrels per day capacity FCCU)	Wet Gas Scrubber	2001
Equilon, Wilmington, CA	25 ppmvd at 0% O <sub>2</sub> , 365-day rolling average (99,000 barrels per day capacity FCCU)	SOx Reducing Catalysts	2001
Equilon, Martinez, CA <sup>(3)</sup>	25 ppmvd at 0% O <sub>2</sub> , 365-day rolling average (155,000 barrels per day capacity FCCU)	SOx Reducing Catalysts	2001
Equilon, Anacortes, WA <sup>(3)</sup>	25 ppmvd at 0% O <sub>2</sub> , 365-day rolling average (145,000 barrels per day capacity FCCU)	Wet Gas Scrubber	2006
Deer Park Refining, Deer Park, TX <sup>(3)</sup>	25 ppmvd at 0% O <sub>2</sub> , 365-day rolling average (340,000 barrels per day capacity FCCU)	Wet Gas Scrubber	2003

Note: 1) The U.S. Environmental Protection Agency RACT/BACT/LAER Clearinghouse; 2) *Assessment of Control Options for Petroleum Refineries in the Mid-Atlantic Region – Final Technical Support Document*. MACTEC Federal Programs, Inc. for Mid-Atlantic Regional Air Management Association (MARAMA), January 31, 2007; 3) *Motiva Enterprises LLC, Equilon Enterprises LLC, and Deer Park Refining Limited Partnership Civil Judicial Settlement*, March 21, 2001; 4) *BP Texas City Site – Texas City, Texas – 2004 Environmental Statement*, June 2005. 5) ~~Permits for Premcor Refining Group Inc., located in Delaware City, DE.~~ Following two landmark settlement agreements in 2001, Valero Premcor a) installed two wet gas scrubbers for the FCCU and fluid coker units; and b) replaced existing scrubber for the HF Alkylation unit with a new, larger unit. The system is designed to achieve 97% emission reduction for the FCCU and 99% reduction for the FCU. The system for FCCU is in

~~operation for 1.5 years, and 2 years SOx emissions from the FCCU, coker unit, and HF Alkylation unit were reported to reduce by an additional 65% for FCU, and continuously achieved 1 ppmv – 2 ppmv SOx, at 0% O2.~~

An extensive study by a refinery in Canada indicates that wet gas scrubbers are commonly used to achieve an emission reduction of 95%, while reducing additives are routinely being used to achieve 85% - 90% reduction.<sup>1</sup> As shown in Table 3-3, it seems that SOx reducing catalysts are typically the choice for FCCUs with average capacity of less than 150,000 barrels feed per day, while wet gas scrubbers are typically the choice for FCCUs with capacity higher than 150,000 barrels per day. Wet gas scrubbers and SOx reducing catalysts will be discussed in details in the sections below.

### 3.3.1 SOx Reducing Catalysts

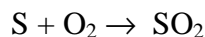
#### 3.3.1.1 Type of Catalysts

Developed in the late 1970s, SOx reducing catalysts were initially alumina based. However, the alumina based catalysts were shown to be susceptible to deactivation. In 1980, it was found that the potential pick-up SO<sub>3</sub> in the regenerator was substantially increased by replacing the pure alumina-based catalysts with a magnesium-aluminate catalysts (1 mole of magnesium per 2 moles of aluminum). In 1990, Akzo Nobel invented hydrotalcite, and hydrotalcite-like, compounds to support up to 3 to 4 moles of magnesium per mole of aluminum. In 1997, Intercat Inc. patented a self-supporting hydrotalcite SOx reducing catalyst, named SOXGETTER<sup>®</sup>, and Grace-Davidson developed a DESOX<sup>®</sup> catalyst with significantly improved performance. In 2000, Intercat Inc. commercialized Super SOXGETTER<sup>®</sup> which is advertised to be 80% better than SOXGETTER<sup>®</sup>, and Grace-Davidson commercialized Super DESOX<sup>®</sup>, 35% better than DESOX<sup>®</sup>.<sup>2, 3</sup>

#### 3.3.1.2 Mechanism for SOx Reduction

In general, SOx reducing catalysts remove SOx from the regenerator flue gas and release the sulfur as H<sub>2</sub>S in the FCCU reactor through a three step mechanism:

In the regenerator, sulfur bearing coke is burned to SO<sub>2</sub>; and in the presence of excess oxygen, a portion of SO<sub>2</sub> is converted to SO<sub>3</sub>



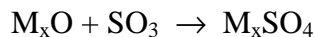
<sup>1</sup> *Reducing Refinery SOx Emissions*. E. Butler, K. Groves, J. Hymanyk of Chevron Canada Limited and M. Maholland, P. Clark, and G. Aru of Intercat Inc. Petroleum Technical Quarterly, Quarter 3, 2006.

<sup>2</sup> *Super DESOX<sup>®</sup>: Providing Benchmark Effectiveness for SOx Reduction*, D. Sellery, Murphy Oil Corporation and B. Riley, GRACE Davison.

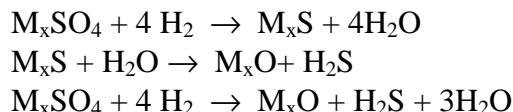
<sup>3</sup> *The Role of Additives in Reducing Fluid Catalytic Cracking SOx and NOx Emissions*, A. Vierheilg and M. Evans, Petroleum and Coal, Volume 45, 3-4, 147-153, 2003.



The magnesium-based reducing catalysts “pick-up”  $\text{SO}_3$  in the regenerator and form magnesium sulfate:



The magnesium sulfate recirculates back to the reactor, and reacts with hydrogen to form either magnesium sulfide and water, or magnesium oxide, and hydrogen sulfide:



The  $\text{H}_2\text{S}$  then exits the FCCU in the dry gas and must be removed by the sulfur recovery units. This increase in  $\text{H}_2\text{S}$ , 5% - 20%, can typically be managed within a refinery’s operations.

### 3.3.1.3 Performance of SOx Reducing Catalysts

Control efficiency of SOx reducing additives depends on many factors such as 1) feed type, 2) starting SOx level, 3) catalyst type, 4) amount of catalysts added, and 5) FCCU’s operating conditions. Manufacturers of SOx reducing catalysts generally use a proprietary computer model to estimate the performance of their products. Typical control efficiencies are reported to be in a range of 70% - 87% from an uncontrolled level as shown in Table 3-45.

**TABLE 3-45**  
**Commercial Results of SOx Reduction Additives**

FCC Type Combustion Mode	Kellogg Total		UOP High Eff, Total		UOP SBS Total		UOP Stacked Partial
	SOXGETTER	DESOX	SOXGETTER	DESOX	SOXGETTER	DESOX	SOXGETTER
<b>Additive</b>							
<b>Feed Quality</b>							
Fresh Feed Rate, MBPD	19.1	18.5	55.5	53.6	64.0	63.0	7.0
Fresh Feed Sulfur, wt%	0.52	0.54	0.71	0.70	1.25	1.49	0.55
<b>Operating Conditions</b>							
Reactor Temperature, °F	1009	1009	1006	999	1005	1005	985
Reactor O <sub>2</sub> , vol%	1.9	1.9	0.9	1.1	1.1	1.3	1.5
Additive Addition, lb/day	728	676	1583	2081	2125	3240	40
<b>Emissions</b>							
Uncontrolled SOx, lb/hr	1181	1086	2046	1895	3100	3853	35
Controlled SOx, lb/hr	154	141	286	303	868	1117	11
Controlled SOx, ppmv	188	179	358	370	575	754	98
<b>Reduction %</b>	<b>87</b>	<b>87</b>	<b>86</b>	<b>84</b>	<b>72</b>	<b>71</b>	<b>70</b>
<b>Additive Efficiency, lb/lb</b>	<b>34</b>	<b>34</b>	<b>27</b>	<b>18</b>	<b>25</b>	<b>20</b>	<b>15</b>

at equivalent SOx red  
level

Reference: *The Role of Additives in Reducing Fluid Catalytic Cracking SOx and NOx Emissions*, A. Vierheilg and M. Evans, Petroleum and Coal, Volume 45, 3-4, 147-153, 2003.

SOx reducing catalysts also reduce PM10. In 2003, during the development of Rule 1105.1 – Reduction of PM10 and Ammonia Emissions from Fluid Catalytic Cracking Units, five refineries in the District experimented with SOx reducing catalysts supplied by Intercat Inc. and Grace-Davidson. Data collected from 2 refineries shown in Table 3-56 shows that with the use of SOx reducing catalysts, SOx and PM<sub>10</sub> emissions could be reduced by approximately 40% - 60%.<sup>4</sup>

**TABLE 3-56**  
**Application of SOx Reducing Catalysts at Chevron and BP**

Refinery	#1	#1	#2	#2
Test Date	Oct-01	Mar-02	Aug-96	Oct-01
SOx Reducing Additives (lbs/day)	0	178	0	1,471
Total PM <sub>10</sub> (lbs/hr)	11.41	6.50	128.89	48.25
SOx (lbs/day)	2,291	1,352	4,553	1,583
Average Period for SOx (days)	16	23	4	24
Percent Reduction	43% for PM <sub>10</sub> 41% for SOx		63% for PM <sub>10</sub> 65% for SOx	

Note: The percent reduction in total PM10 with the SOx reducing additives for Refinery #1 was calculated as follows: % reduction =  $(1 - (6.50/11.42)) \times 100 = 43\%$ . Same approach is used to estimate the percent reduction in total PM10 for Refinery # 2, and the percent reductions in SOx emissions for both refineries. SOx emissions from FCCUs are reported on a daily basis and staff has used an average period from 4 days to 24 days to estimate an average of SOx emissions at these 2 refineries. The information here was presented in the final Staff Report of Rule 1105.1, October 2003.

### 3.3.1.4 Costs and Cost Effectiveness for SOx Reducing Catalysts

Commercial data from Intercat for SOXGETTER<sup>®</sup> have shown that 85% reduction in SOx, resulting in 50 ppmv emissions, can be achieved with an addition rate of 18 lbs SOx per pound of additive. Decreasing emissions to below 25 ppmv reduced the additive efficiency to below 14 lbs SOx per pound of additive. The concentration of SOXGETTER<sup>®</sup> required to reduce emissions below 25 ppmv was slightly greater than 5% by weight of the total catalyst inventory. The relative cost increase to reduce emissions from 50 to 25 ppmv was 31%.

Figure 3-2 was built based on a manufacturer's field and laboratory experience with the additives and provided to staff during the development of Rule 1105.1. In this scenario, if 85% reduction

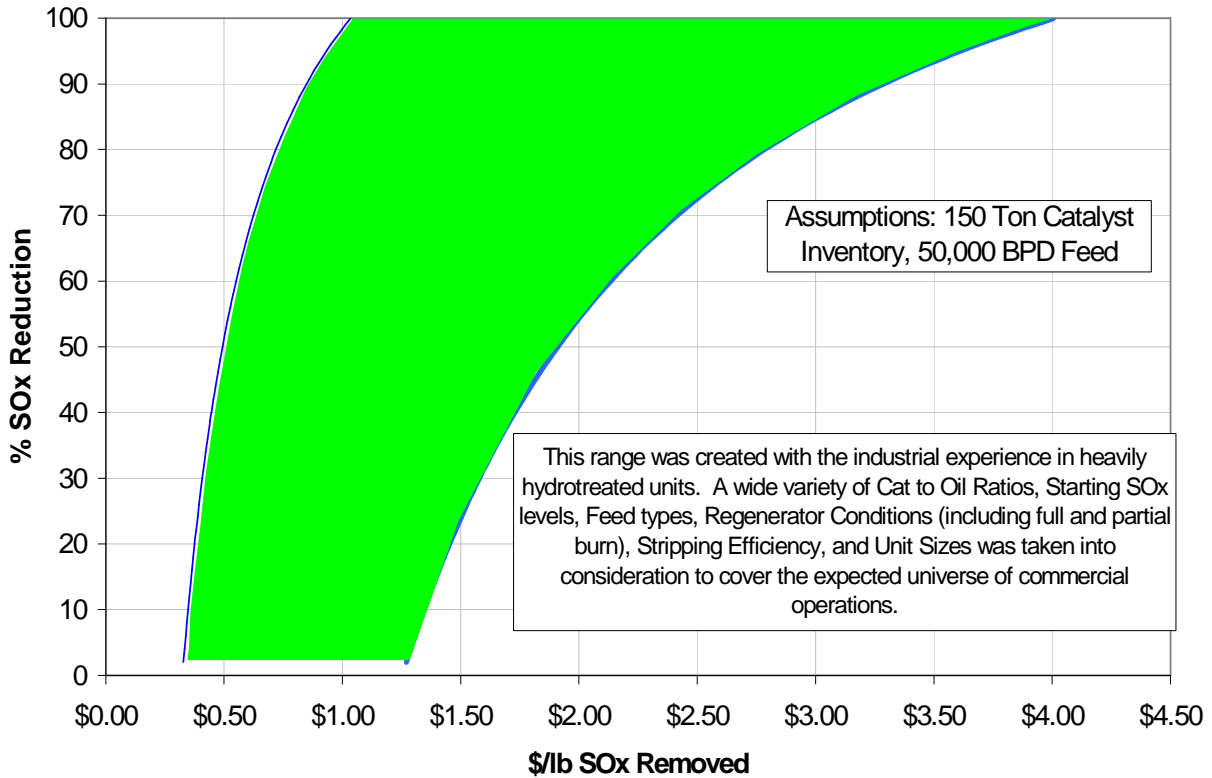
<sup>4</sup> Staff Report of SCAQMD Rule 1105.1 – Reduction of PM10 and Ammonia Emissions from Fluid Catalytic Cracking Unit, October 9, 2003.

is needed to achieve 25 ppmv SOx outlet concentration, the cost effectiveness will be approximately \$6,000 per ton SOx removed.<sup>5</sup>

In other references shown in Table 3-67, a range of \$500 - \$3,000 per ton SOx reduced has been reported in literature.

Through the 2008 Survey Questionnaire, the refineries reported that they currently use Intercat SUPER SOXGETTER and Grace Davison SUPERDESOX at a rate of \$6 - \$8 per pound at an addition rate of 220 lbs/day – 800 lbs/day to the FCCUs.

**FIGURE 3-2**  
**Efficiency of SOx Reducing Additives**



**TABLE 3-67**  
**Cost Effectiveness of SOx Reducing Catalysts**

SOx Level	Cost Effectiveness
10 ppmv – 25 ppmv at 0% O2, 365 day average	In Progress
25 ppmv at 0% O2, 365 day average and	\$500 - \$880 per ton <sup>(1)</sup>

<sup>5</sup> Staff Report of SCAQMD Rule 1105.1 – Reduction of PM10 and Ammonia Emissions from Fluid Catalytic Cracking Unit, October 9, 2003.



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50 ppmv at 0% O <sub>2</sub> , 7-day rolling average	
50% reduction from uncontrolled level	\$2,000 - \$3,000 per ton <sup>(2)</sup>

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Note: 1) *Assessment of Control Options for Petroleum Refineries in the Mid-Atlantic Region – Final Technical Support Document*. Prepared by MACTEC Federal Programs, Inc. for the Mid-Atlantic Regional Air Management Association (MARAMA), January 31, 2007. 2) *Reducing Refinery SO<sub>x</sub> Emissions*. E. Butler, K. Groves, J. Hymanyk of Chevron Canada Limited and M. Maholland, P. Clark, and G. Aru of Intercat Inc. Petroleum Technical Quarterly, Quarter 3, 2006.

### 3.3.2 Wet Gas Scrubbers

Wet scrubbing is used to control both SO<sub>x</sub> and particulate. There are two types of wet scrubbing that are typically used for FCCUs, the caustic-based non-regenerative wet scrubbing and the regenerative scrubbing. Both systems can be used to achieve 25 ppmv SO<sub>x</sub> outlet concentration.

#### 3.3.2.1 Non-Regenerative Wet Gas Scrubbers

Non-regenerative wet scrubbing is a proven control technology for many decades and there are many manufacturers in the U.S. Typically, caustic soda (NaOH) is used as the alkaline absorbing reagent for SO<sub>2</sub>. Other alkaline reagents, such as soda ash and magnesium hydroxide, can also be used. The absorbents capture SO<sub>2</sub>, and convert SO<sub>2</sub> to various types of sulfites and sulfates (NaHSO<sub>3</sub>, Na<sub>2</sub>SO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>). Acid mist (H<sub>2</sub>SO<sub>4</sub>) is also captured. The sulfites and sulfates are later separated in a purge treatment system and the treated water, free of suspended solids, are either discharged or recycled. One example of the caustic-based non regenerative scrubbing system is the proprietary EDV (Electro Dynamic Venturi) scrubbing system offered by BELCO Technologies Corporation, shown in Figure 3-3.<sup>6,7</sup>

An EDV scrubbing system consists of three main modules 1) a spray tower module, 2) a filtering module, and 3) a droplet separator module. The flue gas enters the spray tower module, which is an open tower with multiple layers of spray nozzles. The nozzles supply a high density stream of caustic water which flows countercurrent with the gas flow, circles, encompasses, wets, and saturates the flue gas. Multiple stages of liquid/gas absorption occur in the spray tower module. SO<sub>2</sub> and acid mist are captured and converted to sulfites and sulfates. Large particles in the flue gas are also removed by impaction with the water droplets.

The flue gas saturated with heavy water droplets continues to move up the wet scrubber to the filtering module. In here, the flue gas reaches super-saturation. Water further condenses and agglomeration of fine particles in the gas stream takes place. The size and mass of the fine particulate in the gas stream continue to increase. The flue gas, super-saturated with heavy water droplets, then enters the droplet separator module. The droplet separator module consists of a bank of parallel spin vanes. The heavy, super-saturated, water droplets impinge on the walls of

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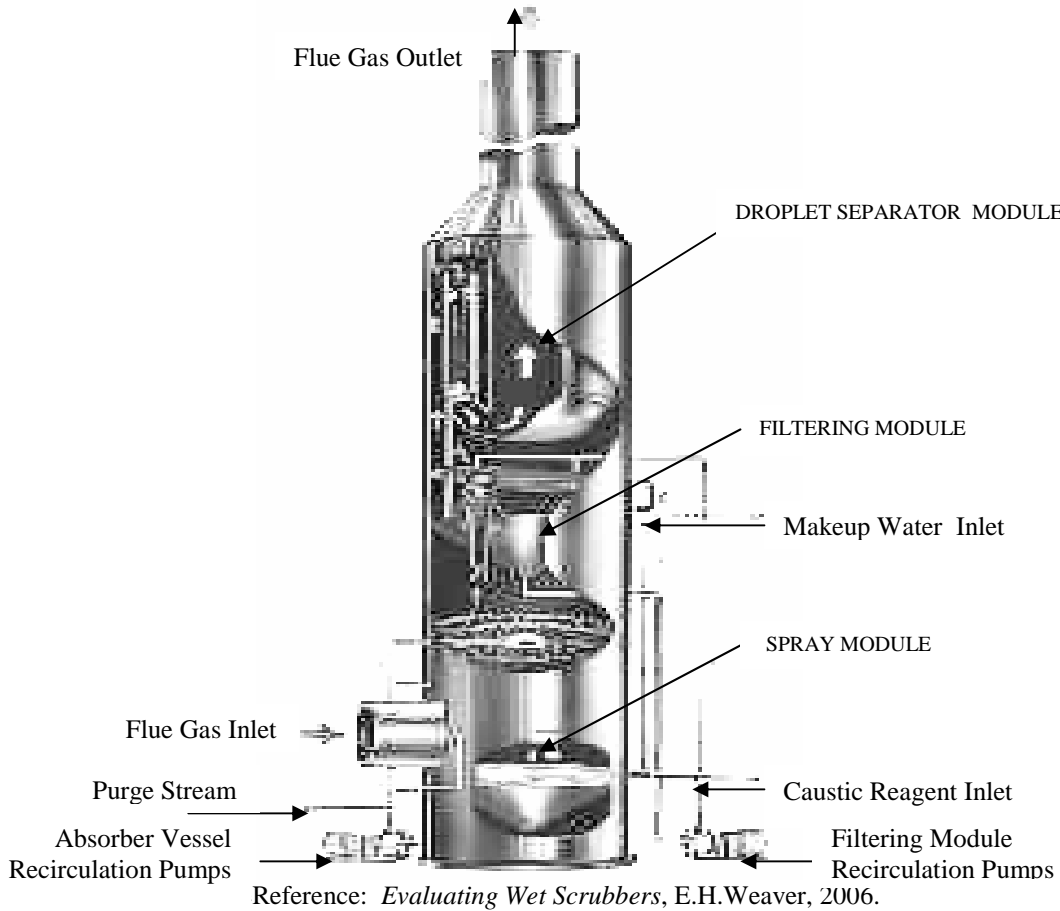
<sup>6</sup> *Evaluating Wet Scrubbers*, Edwin H. Weaver of BELCO Technologies Corporation, Petroleum Technology Quarterly, Quarter 3, 2006.

<sup>7</sup> *A Logical and Cost Effective Approach for Reducing Refinery FCCU Emissions*. S.T. Eagleson, G. Billemeier, N. Confuorto, and E. H. Weaver of BELCO, and S. Singhania and N. Singhania of Singhania Technical Services Pvt., India, Presented at PETROTECH 6<sup>th</sup> International Petroleum Conference in India, January 2005.

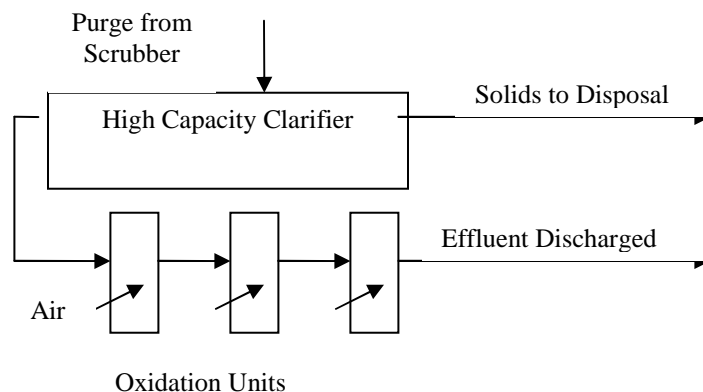
these spin vanes, and are drained to the bottom of the wet scrubber. The filtering module and the droplet separator modules are important components of the wet scrubber to control fine particulate.

The spent caustic water purged from the wet scrubber is typically processed in a purge treatment system shown in Figure 3-4. In the purge treatment unit, a clarifier is used to remove suspended solids which are later disposed. The effluent from the clarifier is oxidized with agitated air. Sulfites are converted to sulfates, and the chemical oxygen demand (COD) is further reduced so that the effluent can be safely discharged to the waste water system.

**FIGURE 3-3**  
**EDV Non-Regenerative Wet Scrubbing System Developed By BELCO**



**FIGURE 3-4**  
**Purge Treatment System**



### 3.3.2.2 Regenerative Wet Gas Scrubbers

The regenerative wet gas scrubbing process removes the SO<sub>2</sub> from the flue gas with a buffer that can be regenerated. The buffer is sent to a regenerative plant where the SO<sub>2</sub> is extracted from the buffer as concentrated SO<sub>2</sub>. The concentrated SO<sub>2</sub> is then sent to a sulfur recovery unit (SRU) to recover sulfur as byproducts, such as liquid SO<sub>2</sub>, sulfuric acid or elemental sulfur. Where the inlet concentrations of SO<sub>2</sub> are high and a significant amount of byproducts can be generated and sold to be used in the fertilizer, chemical, pulp and paper industries, the use of regenerative wet gas scrubber is favored over non-regenerative wet gas scrubber. One example of a regenerative scrubber is the proprietary LABSORB offered by BELCO Technologies Corporation.<sup>8,9</sup>

The LABSORB scrubbing process, as shown in Figure 3-5, uses a patented non-organic aqueous solution of sodium phosphate salts as a buffer. This buffer is made from two common available products, caustic and phosphoric acid. The LABSORB scrubbing system is capable of reducing SO<sub>x</sub> to 25 ppmv. The LABSORP system consists of 1) a quench pre-scrubber, 2) an absorber, and 3) a regeneration section which typically includes a stripper and a heat exchanger.

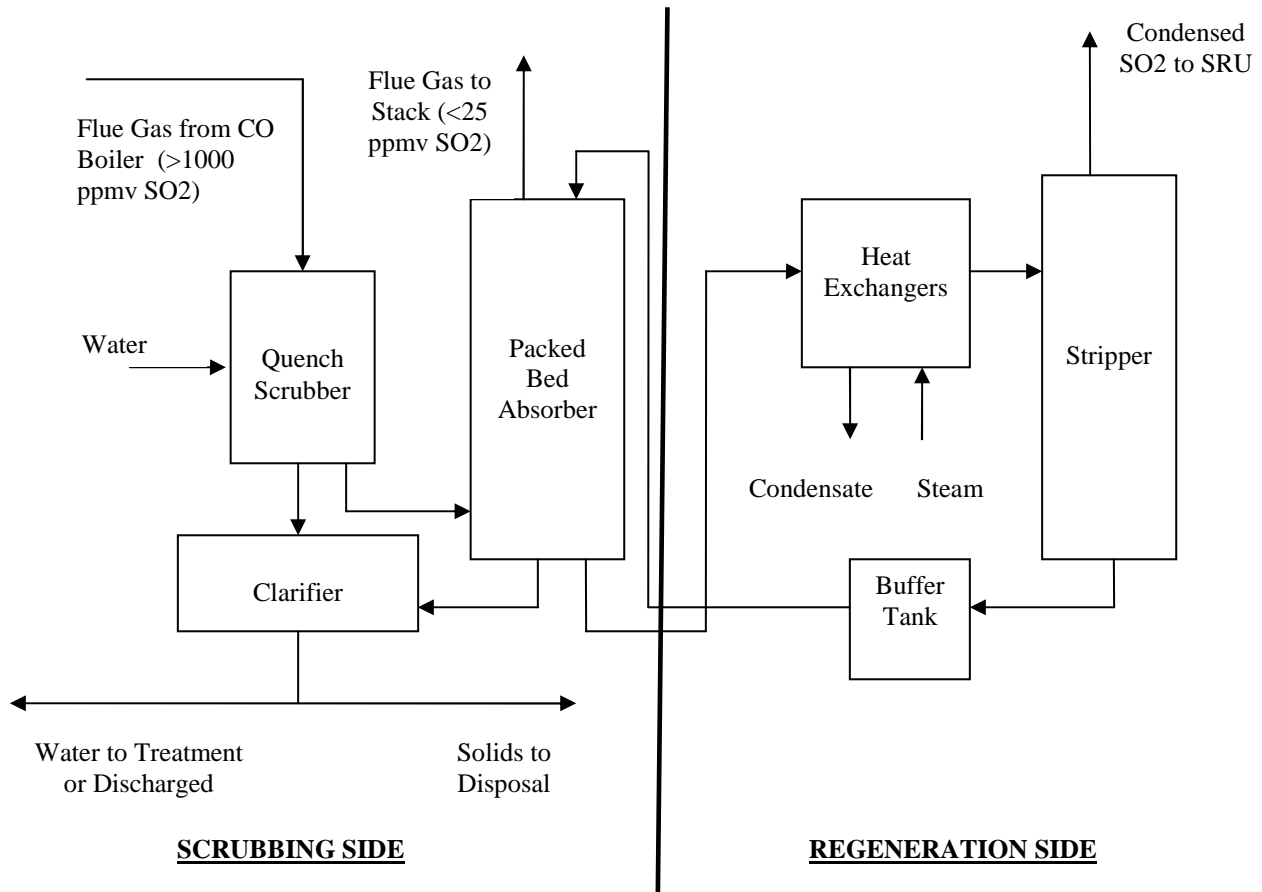
In the scrubbing side of the regenerative scrubbing system, the quench pre-scrubber is used to wash out the large particles carried over, as well as acid components in the flue gas such as HF, HCl and SO<sub>3</sub>. The absorption of SO<sub>2</sub> is carried out in the absorber. The absorber is typically a single high-efficient packed bed scrubber, packed with high-efficient structural packing materials. In some scenarios, such as when the inlet SO<sub>2</sub> concentration is low, a multiple-staged packed bed scrubber, or a spray and plate tower scrubber, is recommended to achieve an outlet concentration of 25 ppmv.

<sup>8</sup> *Evaluating Wet Scrubbers*, Edwin H. Weaver of BELCO Technologies Corporation, Petroleum Technology Quarterly, Quarter 3, 2006.

<sup>9</sup> *A Logical and Cost Effective Approach for Reducing Refinery FCCU Emissions*. S.T. Eagleson, G. Billemeier, N. Confuorto, and E. H. Weaver of BELCO, and S. Singhania and N. Singhania of Singhania Technical Services Pvt., India, Presented at PETROTECH 6<sup>th</sup> International Petroleum Conference in India, January 2005.

In the regenerative side of the regenerative scrubbing system, the SO<sub>2</sub>-rich buffer stream is first heated by steam to vaporize the water and remove it from the buffer. The buffer stream is then sent to a stripper/condenser to separate the SO<sub>2</sub> from the buffer. The buffer free of SO<sub>2</sub> is returned to the buffer mixing tank while the condensed-SO<sub>2</sub> gas stream is sent back to the SRU for further treatment.

**FIGURE 3-5**  
**LABSORB Regenerative Wet Scrubbing System Developed By BELCO**



### 3.3.2.3 Performance for Wet Gas Scrubbers

Many refineries in the U.S. have been installed wet gas scrubbers to meet the U.S. EPA standard of 25 ppmvd SO<sub>2</sub> at 0% O<sub>2</sub>, 365-day rolling average; 50 ppmvd at 0% O<sub>2</sub>, 7-day rolling average as shown in Table 3-3. Two most recent installations of regenerative wet gas scrubbers are described below:

- In 2005, Valero refinery in Delaware City has installed two regenerative wet gas scrubbing systems to reduce SO<sub>x</sub> and particulate emissions for their FCCU and their fluidized coker unit (FCU). The regenerative wet scrubber systems are equipped with BELCO pre-scrubbers and CANSOL packed bed absorbers. The system for the FCCU is designed to treat an inlet flow of 442,400 dscfm, and the system for the FCU is designed to treat 258,200

scfm. The system is designed to reduce 97% emissions from the FCCU, and 99% emissions from the FCU. The systems are in operation since 2006, and have continuously achieved levels of 1 ppmv – 2 ppmv SO<sub>x</sub>, 0% O<sub>2</sub>, overly surpassed the permitted level of ~~The system meets an outlet of~~ 25 ppmv SO<sub>2</sub> at 0% O<sub>2</sub>, 365-day rolling average and 50 ppmvd at 0% O<sub>2</sub>, 7-day rolling average. The capacity of this refinery FCCU is about twice bigger than the largest refinery FCCU in the District.<sup>10</sup>

- A regenerative wet gas scrubbing system was installed for an FCCU at a refinery in Italy, Eni Sannazzaro. The system has been in operation since 2004. The system achieves an outlet concentration of 25 ppmv SO<sub>2</sub>. This refinery has a capacity of 38,000 barrels per day.<sup>11</sup>

### 3.3.2.3 Costs and Cost Effectiveness

The costs for 6 non-regenerative wet scrubbers were provided during the development of SCAQMD Rule 1105.1 in 2003 and is summarized in Table 3-78. The capital costs for a non-regenerative scrubber range from \$9.5 million to \$15 million, and the annual operating costs range from \$320,000 to \$570,000.

**TABLE 3-78**  
**Costs of Wet Gas Scrubbers**

Refinery	Flow Rate (dscfm)	Capital Costs	Operating Costs
#1	24,169 - 94,016	\$10 million	\$370,000
#2	201,913 – 209,652	\$13.8 million	\$560,000
#3	93,813 – 95,359	\$10 million	\$360,000
#4	216,260 – 273,869	\$15 million	\$570,000
#5	116,995 – 135,067	\$12.23 million	\$390,000
#6	86,507 – 87,071	\$9.5 million	\$320,000

Note: The costs were provided by BELCO Technologies Corporation in 2003. The costs include all design, fabrication, supply, installation of a complete EDV system and a new stack, an associated purge treatment unit to meet 25 ppmv SO<sub>2</sub> and 0.005 grain/dscf PM<sub>10</sub>, and all piping/electrical costs within the scrubber battery limit. The costs does not include foundations, ductwork to the scrubber inlet, and piping/instrumentation/electrical, which may add 30% - 50% to the above costs.

A regenerative wet gas scrubber typically costs more than a non-regenerative unit to install. BELCO Inc. estimated that the capital cost of a regenerative system is about 2.4 times the capital cost of a non-regenerative system, primarily due to the additional complexity of the regenerative

<sup>10</sup> Permit for ~~Premcor Refining Group, Inc.'s Delaware City Refinery; (aka Premcor Refining)2005~~ which is now owned by Valero, 2005.

<sup>11</sup> *Evaluating Wet Scrubbers*, Edwin H. Weaver of BELCO Technologies Corporation, Petroleum Technology Quarterly, Quarter 3, 2006.

wet scrubbing system. However, the regenerative system has a significant advantage in annual operating costs because the alkaline absorbing buffer in the regenerative system can be regenerated, low amount of reagents used in the regenerative system, and the byproducts (e.g. elemental sulfur) can be sold. The annual operating costs of a regenerative system are estimated to be about 35% of the annual operating costs of a non-regenerative system as shown in Table 3-89. Table 3-910 presents an estimate for cost effectiveness of the wet gas scrubber, ranging from \$500 - \$3,000 per ton.

**TABLE 3-89**  
**Capital Costs and Annual Operating Costs of Regenerative Wet Gas Scrubbing System**

Type of Costs	Percent Of Costs Comparing to Non-Regenerative WGS
Capital Costs:	240% of Non-Regenerative WGS's
Operating Costs:	
Caustic	18%
Power	35%
Make-Up Water	Less than 5%
Water Discharge	Less than 5%
Solids Disposal	Less than 5%
Operating & Maintenance	20%
Steam	10%
Cooling Water	Less than 5%
Phosphoric Acid	5%

**Reference:** *Evaluating Wet Scrubbers*, Edwin H. Weaver of BELCO Technologies Corporation, Petroleum Technology Quarterly, Quarter 3, 2006.

**TABLE 3-910**  
**Cost Effectiveness for Wet Gas Scrubbers**

SOx Achieved Level	Cost Effectiveness
10 ppmv at 0% O <sub>2</sub> , 365 day average	In Progress
25 ppmv at 0% O <sub>2</sub> , 365 day average	\$500 - \$3,000 per ton <sup>(1)</sup>
50 ppmv at 0% O <sub>2</sub> , 7-day rolling average	

Note: 1) *Assessment of Control Options for Petroleum Refineries in the Mid-Atlantic Region – Final Technical Support Document*. Prepared by MACTEC Federal Programs, Inc. for the Mid-Atlantic Regional Air Management Association (MARAMA), January 31, 2007.

### 3.4 Proposed BARCT Level and Emission Reductions

Based on information gathered up to this time, it is possible that hydrotreating, SO<sub>x</sub> reducing catalysts, wet gas scrubbers, or a combination of the above, could be used to achieve a level of ≤ 10 ppmv SO<sub>2</sub> at 0% O<sub>2</sub>, 365-day rolling average, or ≤ 7 lbs/1000 barrels feed. Staff will continue with the analysis to determine the appropriate BARCT level for the FCCUs in the Basin, estimate potential emission reductions, and conduct a cost effectiveness analysis. These areas will be reported in Part II & III of the ~~Preliminary~~ Draft Staff Report.

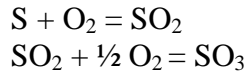


# Chapter 4 – Refinery Boilers and Heaters

## 4.1 Process Description

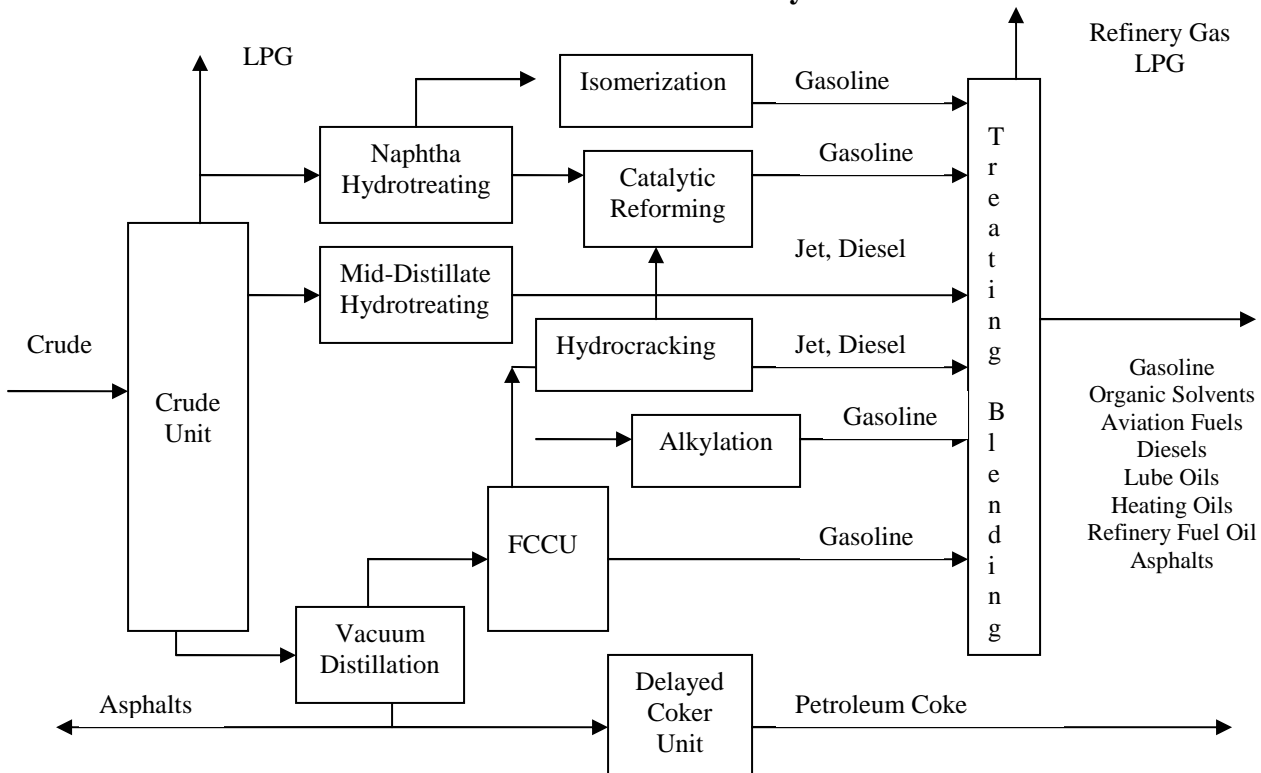
Boilers and heaters are used extensively in almost all of the processes in refinery such as distillation, hydrotreating, fluid catalytic cracking, alkylation, reforming, and delayed coking. Figure 4-1 provides a simplified diagram of the processes where boilers and heaters are used.

The refinery heaters and boilers primarily use refinery gas, one of the product generated at the refinery . As a back-up fuel, most of these boilers and heaters use natural gas. Liquid fuel or solid fuel is rarely used in refinery boilers and heaters. The combustion of sulfur or sulfur compounds in fuel generates sulfur dioxide (SO<sub>2</sub>), with a small amount being further oxidized to sulfur trioxide (SO<sub>3</sub>):



There are approximately 300 boilers and heaters in the refineries. The majority (96%) of these boilers and heaters are classified as major SO<sub>x</sub> sources. Collectively, the boilers and heaters emit about 3 tons per day SO<sub>x</sub>, ranging from 1 lbs to 498 lbs per day from each source, with SO<sub>x</sub> outlet concentration ranging from 7 ppmv – 200 ppmv.

**FIGURE 4-1 - Refinery Processes**



## 4.2 Current Allocations and Emissions

### 4.2.1 Allocations

In 1993, all boilers and heaters at the refineries were provided allocations based on the highest reported fuel usage from 1987 to 1992, and an emission factor of 6.76 lbs SO<sub>x</sub> per million cubic foot of refinery fuel gas. This emission factor was developed based on an assumption that the refinery fuel gas would meet the 40 ppmv standard in Rule 431.1.

**TABLE 4-1**  
**SO<sub>x</sub> Allocations for Refinery Boilers/Heaters**

<b>Facility</b>	<b>Emission Factor (lbs/mmcf)</b>	<b>Tier I Allocations (lbs/year)</b>	<b>Tier I Allocations (tons/day)</b>
A	6.76	190,422	0.26
B	6.76	139,918	0.19
C	6.76	73,779	0.10
D	6.76	101,839	0.14
E	6.76	93,315	0.13
F	6.76	49,859	0.07
		<b>Total</b>	<b>0.89</b>

### 4.2.2 Emissions

In calendar year 2005, the refineries reported a total of 3 tons per day SO<sub>x</sub> emissions from all 300 boilers and heaters currently operated at the refineries. Table 4-2 presents a list of the top 16 emitters in this category which collectively emitted about 1 ton per day of SO<sub>x</sub> in 2005.

**TABLE 4-2**  
**SO<sub>x</sub> Emissions from Top Emitting Boilers/Heaters**

<b>Facility</b>	<b>Device Description</b>	<b>Rating (mmbtu/hr)</b>	<b>2005 Emissions (tons/day)</b>	<b>2006 Emissions (tons/day)</b>	<b>2007 Emissions (tons/day)</b>
B	Crude Heater	550	0.08	0.07	0.07
C	Crude Heater	350	0.10	0.11	0.17
C	Steam Reforming Heater	340	0.09	0.06	0.1
C	Steam Generation Boiler	352	0.06	0.07	0.11
C	Steam Generation Boiler	Not in operation	0.06	0.06	0.11
C	Crude Heater	154	0.04	0.04	0.07
C	Delayed Coking Unit Heater	175	0.04	0.05	0.05
C	Delayed Coking Unit Heater	175	0.04	0.07	0.06
D	Crude Heater	457	0.07	0.11	0.05
D	Hydrogen Plant Furnace	527	0.04	0.05	0.04
D	Steam Generation Boiler	291	0.03	0.02	0.02



**TABLE 4-2 (Continued)**  
**SO<sub>x</sub> Emissions from Top Emitting Boilers/Heaters**

Facility	Device Description	Rating (mmbtu/hr)	2005 Emissions (tons/day)	2006 Emissions (tons/day)	2007 Emissions (tons/day)
E	Coking Unit Heater	252	0.07	0.06	0.06
E	Crude Distillation Heater	175	0.05	0.06	0.06
E	Delayed Coking Unit Heater	168	0.05	0.05	0.05
E	Auxiliary Boiler	139.5	0.04	0.06	0.04
E	Steam Generation Boiler	184	0.04	0.04	0.04
<b>Total 16 Heaters (1 Not in Operation)</b>			<b>0.91</b>	<b>0.98</b>	<b>1.11</b>

Note: The 2005 SO<sub>x</sub> emissions were from SCAQMD database for the period from January 2005 – December 2005. The 2006 and 2007 emissions were reported by the facilities through a Survey Questionnaire distributed by SCAQMD in 2008.

As part of the responses to the 2008 SCAQMD Survey, the refineries reported that the refinery fuel gas is generally hydrotreated with Amine solution to reduce sulfur before being combusted in the refinery heaters and boilers. The sulfur contents in the refinery fuel gas were reported to be in a range of 49 ppmv – 327 ppmv. The SO<sub>x</sub> concentrations in the boilers/heaters' stacks vary from 6.5 ppmv – 44 ppmv

### 4.3 Control Technology

Generally, SO<sub>x</sub> emissions from boilers and heaters can be further reduced by:

- Using lower sulfur fuels;
- Improving efficiency of fuel gas treating system; and
- Using dry or wet gas scrubbers.

#### 4.3.1 Lower Sulfur Fuels

Currently, many boilers and heaters in the U.S. still use solid fuel or liquid fuel. Solid fuel and liquid fuel typically contain higher sulfur content than refinery fuel gas or natural gas, thus the combustion of solid fuel and liquid fuel generates more NO<sub>x</sub> and SO<sub>x</sub> than other types of fuel. Recently, the U.S. EPA has reached various settlement agreements with the refineries to eliminate, or minimize, the use of solid fuel/liquid fuel in all boilers and heaters operated at the refineries.<sup>12, 13</sup> According to these settlement agreements, the use of liquid/solid fuels is only allowed during natural gas curtailment periods.

In the District, boilers/heaters at the refineries typically use refinery gas as primary fuel, and natural gas as a back-up fuel. Liquid fuel, such as diesel, is typically used in internal combustion engines. Diesel fuel, if used, must contain less than 15 ppmw (0.0015%) of sulfur to comply

<sup>12</sup> Motiva Enterprises LLC, Equilon Enterprises LLC, and Deer Park Refining Limited Partnership Civil Judicial Settlement, March 21, 2001.

<sup>13</sup> BP Exploration & Oil Co., Amoco Oil Company, and Atlantic Richfield Company Consent Decree, Civil No. 2:96CV095RL

with the South Coast AQMD Rule 431.2.<sup>14</sup> This requirement is applicable to all non-RECLAIM facilities, as well as RECLAIM facilities, on and after June 1, 2004, however it has not been used to adjust the RECLAIM SO<sub>x</sub> allocations provided in 1993.

However, it should be noted that the allocations provided for the combustion of diesel/liquid fuel in 1993 were approximately 0.043 tons per day, which was less than 0.5% of the total allocations provided to RECLAIM facilities at that time. In addition, the 2005 emissions from the combustion of diesel/liquid fuel in internal combustion engines are only 729 lbs per year (or 0.001 tons per day) which is only about 0.03% of the total emissions from boilers/heaters that use refinery gas. Because the allocations and the 2005 emissions from the combustion solid/liquid fuel in refineries are negligible compared to those generated from the combustion of refinery gas, staff has chosen not to focus in adjusting the allocations of RECLAIM refineries based on the fact that they are required to comply with low sulfur diesel fuel by 2004 at this time.

### **4.3.2 Improving Efficiency of Fuel Gas Treating System**

At the refinery, refinery fuel gas is treated in various acid gas processing units such as an amine or Merox treating unit for removal of sour components (e.g. hydrogen sulfide, carbonyl sulfide, mercaptan, ammonia). Lean amine is generally used as absorbent. At the end of the process, the lean amine is regenerated to form rich amine, and H<sub>2</sub>S is evolved as acid gas which is then fed to the SRUs/tail gas treatment as discussed in Chapter 5. By improving the efficiency of the amine treating unit to recover more sulfur from the inlet acid gas stream, the sulfur content of the outlet refinery fuel gas, and subsequently the SO<sub>x</sub> emissions from boilers and heaters that use these refinery fuel gases can be reduced.

The South Coast AQMD Rule 431.1 limits the sulfur content in the refinery fuel gas to 40 ppmv sulfur.<sup>15</sup> This limit was already incorporated in the RECLAIM allocations and resulted in an emission factor of 6.76 lbs SO<sub>x</sub> per million cubic feet of refinery gas. However, as shown in Table 4-3, the sulfur content in refinery fuel gas may be further reduced to 25 - 35 ppmv at some refineries in the U.S. The outlet SO<sub>x</sub> concentrations from boilers/heaters may also be limited to less than 20 ppmv. The costs of modifying an acid gas processing unit may vary widely on a case-by-case basis, therefore staff has chosen not to analyze this control option at this time, and may need to discuss this control option in details with the refineries at a later date.

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<sup>14</sup> SCAQMD Rule 431.2 – Sulfur Contents of Liquid Fuels, Amended September 15, 2000.

<sup>15</sup> SCAQMD Rule 431.1 – Sulfur Contents of Gaseous Fuels, Amended June 12, 1998.

**TABLE 4-3  
Standards for Boilers and Heaters**

<b>Company</b>	<b>Description of Boilers/Heaters</b>	<b>SO<sub>x</sub> Standard</b>
Marathon Petroleum Co LLC., Garyville Refinery, Louisiana <sup>(1)</sup>	Crude heaters, 368 mmbtu/hr Hydrogen reformer heater, 1412 mmbtu/hr Platformer heaters, 474 mmbtu/hr & 542 mmbtu/hr Vacuum tower heaters, 155 mmbtu/hr Naphtha hydrotreater charge heater, 75.7 mmbtu/hr Naphtha hydrotreater reboiler heater, 138 mmbtu/hr Boiler, 526 mmbtu/hr	Inlet standard: 25 ppmv as H <sub>2</sub> S, inlet concentration of refinery fuel gas, annual average.
Arizona Clean Fuels Yuma LLC, Yuma AZ. (Facility has not yet built.) <sup>(1)</sup>	Atmospheric crude charge heater, 346 mmbtu/hr Vacuum crude charge heater, 101 mmbtu/hr Hydrocracker charge heater, 70 mmbtu/hr Hydrocracker main fractionator heater, 211 mmbtu/hr Naphtha hydrotreater charge heater, 21 mmbtu/hr Catalytic reforming charge heater, 122 mmbtu/hr Catalytic reforming interheater #1, 192 mmbtu/hr Catalytic reforming interheater #2, 129 mmbtu/hr Catalytic reforming debutanizer reboiler, 23 mmbtu/hr Distillate hydrotreater charge heater, 25 mmbtu/hr Distillate hydrotreater splitter reboiler, 117 mmbtu/hr Butane dehydrogenation reactor heater, 311 mmbtu/hr Butane conversion isostripper reboiler, 222 mmbtu/hr Delayed coking charge heaters, 99 mmbtu/hr	Inlet standard: 35 ppmv, as H <sub>2</sub> S, inlet concentration of refinery fuel gas.
Equilon <sup>(2)</sup>	<del>All boilers and heaters firing refinery fuel gas. Solid and liquid fuel firing is limited to a maximum.</del>	Outlet standard: 20 ppmv SO <sub>2</sub> at 0% O <sub>2</sub> , 3 hour rolling average; or 0.1 grains of H <sub>2</sub> S/dscf
Toseco Refining Company <sup>(3)</sup>	Hydrogen Reforming Furnace, 460 mmbtu/hr	Outlet standard: 11.1 lb/hr SO <sub>x</sub> . Outlet measured <6.7 ppmv SO <sub>x</sub> at 3% O <sub>2</sub> , 1 hour average, which was about 4 lbs/hr

Note: 1) The U.S. Environmental Protection Agency RACT/BACT/LAER Clearinghouse. Staff is in the process of gathering additional information (e.g. permits) from these facilities to assess whether or not the limit of 25 ppmv and 35 ppmv is for total sulfur measured as H<sub>2</sub>S, or just for H<sub>2</sub>S levels alone; 2) Motiva Enterprises LLC, Equilon Enterprises LLC, and Deer Park Refining Limited Partnership Civil Judicial Settlement, March 21, 2001. 3) CARB BACT Clearinghouse

### 4.3.3 Flue Gas Scrubbers

While the first two control options are aiming at reducing the sulfur content of fuel before it is combusted, flue gas scrubbing is aiming at reducing SO<sub>x</sub> emissions in the flue gas after it exits the boilers and heaters. Literature contains extensive information about these technologies.<sup>16, 17</sup>

#### 4.3.3.1 Dry Scrubbers

Dry scrubbers include 1) spray dryer scrubbers and 2) dry injection scrubbers. In dry scrubbers, a dry calcium and sodium based alkaline powered sorbent is used to absorb SO<sub>2</sub>. A spray dryer scrubber refers to a configuration where the reaction between SO<sub>2</sub> and the dry sorbent takes place in a dedicated reactor (or scrubber), whereas in the dry injection scrubber, the sorbent is injected directly into the existing boiler/heater or the ducting system of the boiler/heater.

In the dry scrubbers, high temperatures (1800 – 2000 degree F) are needed to decompose the sorbent into porous solids with high adsorbing surface area. Several injection ports may be required for even distribution of dry sorbent in the boilers/heaters or ductwork. Cyclones and ESPs are typically used downstream of a dry scrubber to remove the particulate formed in the process. Dry injection scrubbers can achieve about 50% - 80% removal efficiency, whereas spray dryer scrubbers can achieve about 80% – 90%. Dry scrubbers are mostly applicable to small and medium size boilers/heaters with low level of inlet SO<sub>x</sub>.

#### 4.3.3.2 Wet Scrubbers

In wet scrubbers, aqueous slurry of limestone, lime, or other proprietary sorbent is used to absorb SO<sub>2</sub>. A wet scrubber includes a spray tower which is generally followed by a mist eliminator. The flue gas enters a spray tower, where it is impacted with aqueous lime or limestone slurry for SO<sub>2</sub> absorption. Particulate formed in the spray tower falls to the bottom of the spray tower, where it is collected and recycled back to the scrubber system or disposed. The scrubbed flue gas is then sent to a mist-eliminator to remove any entrained particulate droplets. Wet scrubbers are about 90% - 98% efficiency in removing SO<sub>x</sub> depending on the type of sorbent used.

As discussed in Chapter 3, Section 3.3.2, wet scrubbers are used extensively to control SO<sub>x</sub> and PM from FCCUs at several refineries in the U.S. A wet scrubber designed by BELCO includes a spray module with two additional modules, a filtering module and a droplet separator module, to remove fine particulate. This scrubber has been used to achieved an outlet concentration of 25

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<sup>16</sup> *Assessment of Control Options for Petroleum Refineries in the Mid-Atlantic Region – Final Technical Support Document*. Prepared by MACTEC Federal Programs, Inc. for the Mid-Atlantic Regional Air Management Association (MARAMA), January 31, 2007.

<sup>17</sup> *Assessment of Control Technology Options for BART-Eligible Sources – Steam Electric Boilers, Industrial Boilers, Cement Plants, and Paper and Pulp Facilities*. Northeast States for Coordinated Air Use Management (NESCAUM) in partnership with the Mid-Atlantic Northeast Visibility Union (MANE-VU), March 2005.

ppmv of SO<sub>x</sub> from FCCUs. Boilers/heaters are expected to achieve a level of 20 ppmv or lower as shown in Table 4-3.

### 4.3.3.3 Costs and Cost Effectiveness

Cost effectiveness for wet gas scrubbers has been estimated to be \$7,674,700 - \$45,384,400 per ton depending on the size of the scrubbers, inlet SO<sub>x</sub>, and amount of emissions reduced.<sup>18</sup> Using a wet gas scrubber may allow the refinery to combust higher sulfur fuel; and since higher sulfur fuel costs less than low sulfur fuel, this can result in a savings in annual operating costs. BELCO estimated that using a EDV® wet gas scrubber with caustic soda (NaOH) as a scrubbing agent for a 198 mmbtu/hr vacuum distillation process heater burning high sulfur fuel of 150 ppmv – 200 ppmv could generate a saving of \$1 - \$2.8 million dollars per year.<sup>19</sup>

**TABLE 4-4**  
**Cost Effectiveness for Wet Scrubbers**

<b>Efficiency</b>	<b>Cost Effectiveness</b>
90-99.9%	\$7,674,700 - \$45,384,400 per ton
99%+	\$1 - \$2.8 million dollars annual savings for a 198 mmbtu/hr heater

## 4.4 Proposed BARCT Level and Emission Reductions

Improving the fuel gas treating system or using flue gas scrubbers could reduce the SO<sub>x</sub> emissions from boilers/heaters. Further analysis is required to assess the appropriate BARCT level (e.g.  $\leq 20$  ppmv SO<sub>x</sub>, or  $\leq 25$  ppmv sulfur content). Staff will continue the BARCT analysis, estimate emission reductions, and cost effectiveness, and will include the findings in Part II and III of the Preliminary Draft Staff Report.

<sup>18</sup> *Assessment of Control Options for Petroleum Refineries in the Mid-Atlantic Region – Final Technical Support Document*. Prepared by MACTEC Federal Programs, Inc. for the Mid-Atlantic Regional Air Management Association (MARAMA), January 2007.

<sup>19</sup> *Controlling Fired Process Heater Emissions to Reduce Fuel Costs and Improve Air Quality*, S.T. Eagleson and N. Confuorto of BELCO, S.Singhania and N. Singhania of Singhania Technical Services Pvt., and R. John of Lisha Engineering Co., Presented in the Petrotech 7<sup>th</sup> International Oil & Gas Conference, January 24, 2007

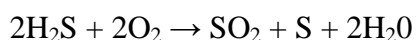


## Chapter 5 - Sulfur Recovery – Tail Gas Treatment Units

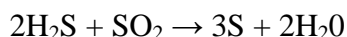
### 5.1 Process Description

A typical sulfur recovery system at the refineries include a sulfur recovery unit (Claus unit) followed by a tail gas treatment unit (e.g. Amine treating) to maximize the removal of H<sub>2</sub>S.

The Claus sulfur recovery unit, as shown in Figure 5-1, consists of a reactor, converters and condensers. The two reactions proceed in the Claus sulfur recovery unit are exothermic. The first reaction occurs in the Claus reactor, where a portion of H<sub>2</sub>S reacts with air to form SO<sub>2</sub>.



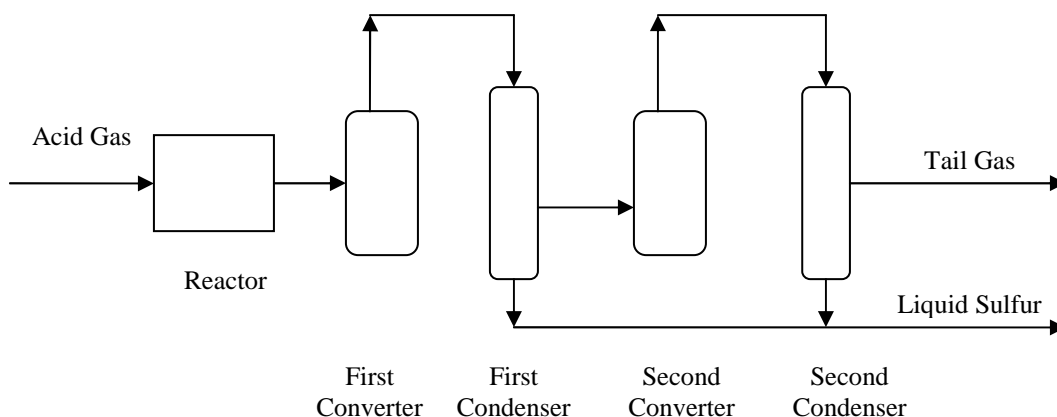
The second reaction takes place in the catalytic converter where SO<sub>2</sub> reacts with H<sub>2</sub>S to form liquid elemental sulfur.



Side reactions also occur which produce carbonyl sulfide (COS) and carbon disulfide (CS<sub>2</sub>), which have presented problems in many Claus plant operations due to the fact that they can not be easily converted to elemental sulfur and carbon dioxide,

Liquid sulfur is recovered after the final condenser. Two converters and two condensers in series generally remove 95% of the sulfur in the incoming acid gas. Some of the newer sulfur recovery units have three to four sets of converters and condensers.

**FIGURE 5-1**  
**Two Stage Claus Sulfur Recovery Process**



To recover the remaining sulfur compounds in the tail gas, the tail gas is sent to a tail gas treatment process, such as amine, diethanol amine (DEA), SCOT, Wellman-Lord, and FLEXSORB.

Figure 5-2 shows a simplified diagram of SCOT tail gas treatment process. The sulfur compounds in the tail gas are reduced in a catalytic reactor to  $H_2S$ . The  $H_2S$  is absorbed in the amine (or other absorbent) in the  $H_2S$  absorber, steam-stripped from the absorbent solution in the  $H_2S$  stripper, concentrated, and recycled back to the front end of the sulfur recovery unit. This approach typically increases the overall sulfur recovery efficiency of the Claus unit to 99.8% or higher. However, the fresh acid gas feed rate to the sulfur recovery unit is reduced by the amount of recycled stream, which reduces the capacity of the sulfur recovery unit. The residual  $H_2S$  in the treated gas from the absorber is typically vented to a thermal oxidizer where it is oxidized to  $SO_2$  before emitting to the atmosphere.

**FIGURE 5-2**  
**Tail Gas Treatment – SCOT Process**

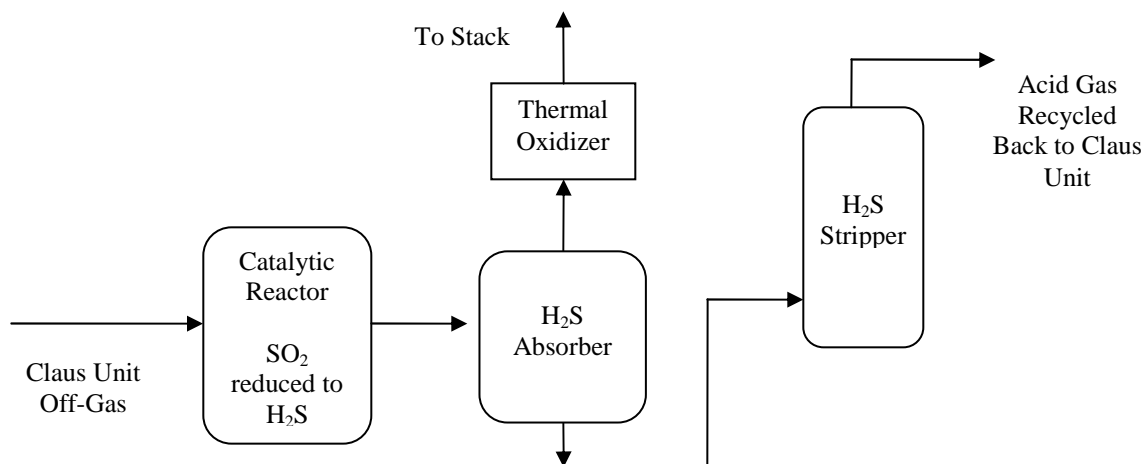
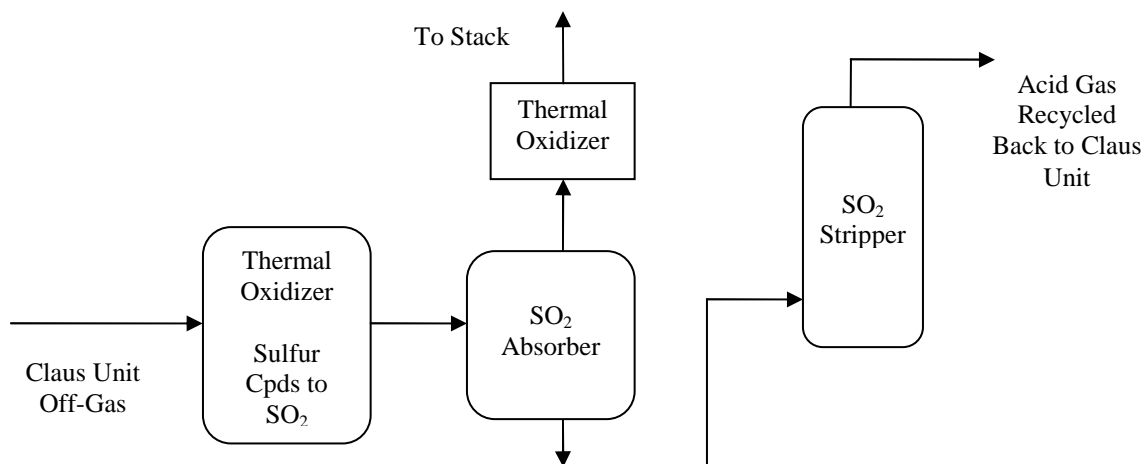


Figure 5-3 shows a simplified diagram of Wellman-Lord tail gas treatment process. The sulfur compounds in the tail gas are first incinerated with air to oxidize to  $SO_2$ . After the incinerator, the tail gas enters a  $SO_2$  absorber, where the  $SO_2$  is absorbed in typically sodium sulfite ( $Na_2SO_3$ ) solution to form sodium bisulfite ( $NaHSO_3$ ) and sodium pyrosulfate ( $Na_2S_2O_5$ ). The absorbent rich in  $SO_2$  is then stripped, and the  $SO_2$  is recycled back to the Claus gas. The residual sulfur compounds in the treated tail gas from the  $SO_2$  absorber is typically vented to a thermal oxidizer where it is oxidized to  $SO_2$  before emitting to the atmosphere.

**FIGURE 5-3**  
**Tail Gas Treatment - Wellman-Lord Process**



## 5.2 Current Allocations and Emissions

### 5.2.1 Allocations

In 1993, the facilities were issued emission allocations for their sulfur recovery - tail gas treatment unit based on the highest reported emissions from 1988 – 1992. The emissions allocated to each unit are listed in Table 5-1. The total Tier I allocations provided were 1.61 tons per day.

**TABLE 5-1**  
**SO<sub>x</sub> Allocations for Sulfur Recovery -Tail Gas Treatment Units**

Facility	Process	Peak Year	Tier I Allocations (lbs/year)	Tier I Allocations (tons/day)
B	Tail Gas Unit	1990	353,992	0.48
A	Inorganic Chemicals	1992	280,670	0.38
A	Sour Water Oxidizer	1992	2,328	0.00
A	Sulfur Plant	1992	65,341	0.09
A	Tail Gas Unit	1992	31,343	0.04
D	KCR Process	1992	6,904	0.01
D	Merox Process	1992	1,599	0.00

**TABLE 5-1 (Continued)**  
**SOx Allocations for Sulfur Recovery -Tail Gas Treatment Units**

<b>Facility</b>	<b>Process</b>	<b>Peak Year</b>	<b>Tier I Allocations (lbs/year)</b>	<b>Tier I Allocations (tons/day)</b>
D	Tail Gas Unit	1992	6,008	0.01
D	Tail Gas Unit	1992	50,587	0.07
G	Tail Gas Unit	1991	14,934	0.02
CC	Sour Water Coker	1988	12,360	0.02
CC	Sour Water Oxidizer	1988	12,360	0.02
CC	Sulfur Plant	1988	87,477	0.12
C	Tail Gas Unit	1988	6,500	0.01
E	Mericher Alkyd Feed	1991	250,983	0.34
			<b>Total</b>	<b>1.61</b>

## 5.2.2 Emissions

Since sulfur recovery - tail gas treatment unit with thermal oxidizers are classified as major sources in RECLAIM, the SOx emissions from these units are monitored with CEMS and reported on a daily basis to the District. The total annual emissions for 2005, 2006, and 2007, 0.96 tpd, 1.02 tpd and 0.96 tpd respectively from these units are presented in Table 5-2.

The sulfur recovery - tail gas treatment units at RECLAIM facilities are not subject to any specific concentration or emission rate standards. RECLAIM facilities are given the flexibilities to operate their equipment anyway they want provided that the total emissions from the facility are below facility emission caps. The allocations provided to these units since 1993 have not been adjusted even though there may have emerging technologies that can be used to further reduce SOx emissions from these units. Comparing the allocations provided in 1993 at 1.61 tons per day with the 2005 reported emissions at 0.96 tons per day, it seems that the sulfur recovery - tail gas treatment units at RECLAIM facilities have been slightly improved since 1993 provided that their capacity has not been changed.

Through the 2008 Survey, the refineries reported that their SRUs' capacity ranges from 90 long tons per day – 270 long tons per day. The refineries have been using more than one Claus units with the technologies such as SUPERCLAUS, FLEXSORB, or WELLMAN LORD to recover approximately 95% - 99.99% sulfur in their SRUs and tail gas treatment. All six refineries have thermal oxidizers at the end of their tail gas treatment units. A refinery reported that they would only vent the tail gas to incinerators when needed to meet the requirement of NSPS 40 CFR Part 60, Subpart J. The stack average SOx concentrations at the outlet of the thermal oxidizers vary widely from 20 ppmv at 0% O2 for Refinery E, 26 ppmv for Refinery D, 59 ppmv – 77 ppmv for Refinery A, 98 ppmv – 150 ppmv for Refinery B, and 98 ppmv for Refinery F

**TABLE 5-2**  
**SO<sub>x</sub> Emissions from Sulfur Recovery – Tail Gas Treatment Units**

Facility	Device Description	Rating (mmbtu/hr)	2005 Emissions (tons/day)	2006 Emissions (tons/day)	2007 Emissions (tons/day)
B	Thermal oxidizer #2	44.5	0.16	0.22	0.26
B	Thermal oxidizer #1	39.5	0.15	0.12	0.11
A	Thermal oxidizer #70	58	0.10	0.14	0.12
A	Thermal oxidizer #20	30	0.09	0.09	0.08
A	Thermal oxidizer #10	30	0.06	0.08	0.06
C	Tail gas incinerator #1	19.5	0.01	<del>0.02</del> 0.00	0.01
C	Tail gas incinerator #2	19.5	0.01	<del>0.00</del> 0.02	0.01
CC	<u>Thermal incinerator</u>	NA	<del>NA</del> 0.05	0.10	0.09
CC	<u>Thermal incinerator</u>	NA	<del>NA</del> 0.02	0.01	0.02
D	Tail gas oxidizer	100	0.15	0.21	0.17
E	Incinerator for SRU	52	0.05	NA	NA
E	Incinerator for SRU	45	0.02	NA	NA
F	Thermal oxidizer	35.8	0.16	0.03	0.03
			<b>0.96</b> <b>1.03</b>	<b>1.02</b>	<b>0.96</b>

Note: The 2005 SO<sub>x</sub> emissions were from SCAQMD database for the period from January 2005 – December 2005. The 2006 and 2007 emissions were reported by the facilities through a Survey Questionnaire distributed by SCAQMD in 2008.

### 5.3 Control Technology

The main purpose of the Claus sulfur recovery - tail gas treatment units is to recover sulfur. Afterwards, the treated gas is vented to a thermal oxidizer to oxidize the remaining H<sub>2</sub>S. The Claus sulfur recovery, tail gas treatment and thermal oxidizer systems in the District generally have recovery efficiency of about 95% - 99.99% to meet NSPS 40 CFR Part 60, Subpart J limit and SCAQMD Rule 468 limit (e.g. 250 ppmv SO<sub>2</sub> with the use of thermal oxidizers, or 10 ppmv H<sub>2</sub>S without the use of thermal oxidizers). The three main strategies that can be employed to further reduce SO<sub>2</sub> emissions from these units are 1) to increase the efficiency of the sulfur recovery unit, 2) to improve the efficiency of the tail gas treatment processes, and 3) to use a wet gas scrubber as an alternative for the thermal oxidizer.

#### 5.3.1 Increase Efficiency of the Sulfur Recovery Unit

##### 5.3.1.1 SELECTOX

The SELECTOX catalyst is used in the first stage of the Claus unit to promote the oxidation of H<sub>2</sub>S to SO<sub>2</sub> without the use of a flame. SELECTOX catalyst has helped to increase the efficiency of sulfur recovery unit from 90% to 97%. SELECTOX has been used in San Joaquin

Refinery located in Bakersfield, California.<sup>20</sup> Other catalysts such as Criterion catalysts have been used to increase the sulfur recovery efficiency from a typical 96% - 97% to 99.8% - 99.9%. Testing on the tail gas unit at the Motiva Enterprises' Port Arthur refinery demonstrated that the stack SO<sub>2</sub> remained in the 22 ppmv – 28 ppmv range, which was only about 10% of the permitted maximum 250 ppmv required by NSPS, 40 CFR Part J.<sup>21</sup>

### **5.3.1.2 SUPER-CLAUS®**

The SUPERCLAUS sulfur recovery unit is similar to the Claus unit but contains three to four catalytic converters. The first two or three catalytic converters use the Claus catalysts, while the last reactor uses a selective oxidation catalyst that highly selective and oxidize H<sub>2</sub>S to sulfur. The efficiency of sulfur recovery is about 99%.

## **5.3.2 Increase Efficiency of Tail Gas Unit**

### **5.3.2.1 SCOT Tail Gas Unit**

SCOT stands for Shell Claus Off-gas Treating, which is the most common tail gas treatment system. Tail gas from the Claus unit is contacted with hydrogen and reduced in the hydrotreating reactor to form H<sub>2</sub>S and water in the presence of a cobalt/molybdenum or alumina catalyst. The gas is then cooled and enters an amine absorber where it is contacted with monoethanolamine (MEA) or diethanolamine (DEA), or triethanolamine (TEA) to generate a rich amine stream. The rich amine stream is then desorbed in a stripper, where a lean amine stream is regenerated and recycled to the absorber, while an H<sub>2</sub>S gas stream is sent back to the Claus unit. This technology has been used by several refineries in the District as reported through the 2008 Survey.

### **5.3.2.2 Sulfreen Tail Gas Unit**

The Sulfreen process is a catalytic tail gas process that adds two or three Sulfreen reactors to treat the tail gas. Alumina catalyst is used to remove additional sulfur. Activated titanium oxide is used to remove COS and CS<sub>2</sub>. Any remaining H<sub>2</sub>S leaves the reactors is oxidized in the final stage. The recovering efficiency of the Sulfreen process is 99 – 99.9%.

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<sup>20</sup> *Sulfur Technology, Capability and Experience.* WorleyParsons.

<sup>21</sup> *Catalysts for Lower Temperature Tail Gas Unit Operation.* S. Massie and C. Wilson of Criterion Catalysts & Technologies, presented at the Brimstone Sulfur Recovery Symposium, Vail, Colorado, September 2005.

### 5.3.2.3 Beaven Process

The Beaven process uses quinine solution to absorb  $H_2S$  in the tail gas. The absorbed  $H_2S$  is then oxidized to form a mixture of elemental sulfur and hydroquinone. Hydroquinone is converted back to quinone. Before entering the absorber,  $COS$  and  $CS_2$  in the tail gas can also be eliminated by the use of cobalt molybdate catalyst in a reactor located prior to the absorber. The recovering efficiency of the Beaven process is 99% – 99.9%.

### 5.3.2.4 Stretford Process

The Stretford process uses a hydrotreating reactor to convert  $SO_2$  in the tail gas to  $H_2S$ , and then contacts  $H_2S$  with Stretford solution in a liquid-gas absorber. The Stretford solution contains a mixture of vanadium salt, anthraquinone disulfonic acid (ADA), sodium carbonate, and sodium hydroxide. The vanadium salt acts as a catalyst to convert  $H_2S$  into elemental sulfur. The recovering efficiency of the Stretford process is about 99%.

### 5.3.2.5 FLEXSORB ®

The FLEXSORB process were developed by the ExxonMobil Research and Engineering as alternative to the MDEA amine treatment process. The process uses a number of FLEXSORB solvents include the SE, SE Plus, SE hybrid, and the PS solvents. The solvents are designed to selectively absorb and convert  $H_2S$ , organic sulfur to elemental sulfur. The efficiency of FLEXSORB is about 99.9+%. This technology has been used by one refinery in the District as reported through the 2008 SCAQMD Survey.

### 5.3.2.6 PRO-Claus

The Parsons RedOx Claus (PROClas) unit is a dry catalytic process that contains three additional stages, a reduction and two oxidation stages. In a reduction stage, a highly selective  $SO_2$  reduction catalyst developed by Lawrence Berkeley National Laboratory is used to accelerate the reduction of  $SO_2$  to elemental sulfur. After this stage, the remaining  $H_2S$  is oxidized to form elemental sulfur under the presence of a Parsons Hi-Activity selective oxidation catalyst, and then it is sent to a thermal oxidizer to complete the oxidation process. An overall sulfur recovery efficiency of all three stages is 99.5%.

### 5.3.2.7 LO-CAT

LO-CAT is a liquid redox tail gas treatment capable of recovering 99.9+% with or with the use of a proprietary Mobile Bed Absorber (MBA) where  $H_2S$  and  $SO_2$  are absorbed into a circulating solution and converted to elemental sulfur in the presence of a chelated-iron catalyst. The solution leaving the MBA is then oxidized. Exhaust gas from the MBA is vented to the atmosphere and contains less than 10 ppmv  $H_2S$ .

Table 5-3 provides a summary of the processes described above.

**TABLE 5-3**  
**Control Efficiency of Sulfur Recovery – Tail Gas Treatment Process**

Process	Efficiency
Typical Claus with tail gas treatment and incinerators	90% - 95% (<250 ppmv)
Selectox catalyst for Claus Unit	97%
SUPERCLAUS® for Claus Unit	99%
SCOT for Tail Gas Treatment	99%
Sulfreen for Tail Gas Treatment	99% - 99.9+%
Beaven for Tail Gas Treatment	99% - 99.9+%
Stretford Tail Gas Treatment	99%
FLEXSORB Tail Gas Treatment	99.9+%
PRO-Claus Tail Gas Treatment	99.5%
LO-CAT Tail Gas Treatment	99.9+%

Reference: *Assessment of Control Options for Petroleum Refineries in the Mid-Atlantic Region – Final Technical Support Document*. Prepared by MACTEC Federal Programs, Inc. for the Mid-Atlantic Regional Air Management Association (MARAMA), January 31, 2007.

### 5.3.3 Wet Gas Scrubber

As described above, typically in the District, the tail gas from the Claus sulfur recovery unit is sent to an amine treatment process, which absorbs H<sub>2</sub>S, produces a concentrated H<sub>2</sub>S stream, and recycles the concentrated H<sub>2</sub>S stream to the front end of the SRU. The residual H<sub>2</sub>S in the treated gas is typically vented to a thermal oxidizer where H<sub>2</sub>S is oxidized to SO<sub>2</sub> before emitting to the atmosphere. This approach typically increases the overall sulfur recovery efficiency of the Claus sulfur recovery unit, however has the tendency to reduce the amount of fresh acid gas stream that could potentially be treated by the Claus sulfur recovery unit.

As an alternative to this process, the tail gas from the Claus unit is first oxidized to SO<sub>2</sub>. The SO<sub>2</sub> is then captured by alkaline agent (e.g. sodium hydroxide caustic solution) in a wet gas scrubber, and the residual SO<sub>2</sub> not captured in the scrubber is discharged to the atmosphere. With this approach, there is no concentrated H<sub>2</sub>S stream recycle to the front end of the SRU, and the overall sulfur recovery/removal efficiency is increased to 99.95%, above the efficiency of the current Claus SRU-Tail Gas Treatment systems in the District.<sup>22</sup> Two types of wet gas scrubbers that have been installed and used by the refineries in the U.S. are described in details below.

<sup>22</sup> *Improving Sulfur Recovery Units*, E. Juno of Sinclair Oil Corporation, S.F. Myer and C. Kulczycki of MECS, and N. Watts of CEntry Constructors and Engineers, Petroleum Technical Quarterly, Quarter 3 of 2006.



### 5.3.3.1 DynaWave Non-Regenerative Scrubber

Wet gas scrubbing technique is currently used at two refineries in Wyoming, the Sinclair Oil refinery, rated 72,000 barrels per day, and the Casper refinery, rated at 22,500 barrels per day. The scrubbers used at these two refineries are manufactured by DynaWave and use caustic (NaOH) as a scrubbing agent.

DynaWave scrubber can utilize other sodium based agents such as soda ash ( $\text{Na}_2\text{CO}_3$ ), or calcium based agents such as lime (CaO) or limestone ( $\text{CaCO}_3$ ), however Sinclair Oil refinery and Casper refinery have selected caustic (NaOH) because:

- Caustic was available as a 50% solution which could be pumped directly to the scrubber without further dilution or mixing. Soda ash or calcium based agents are only readily available as a powder and they would require an installation of a reagent preparation station.
- The reaction between  $\text{SO}_2$  and caustic (NaOH) are relatively fast compared to the reaction of  $\text{SO}_2$  with calcium based reagents. The products, sodium sulfite ( $\text{NaHSO}_3$ ) or sodium bisulfite salts ( $\text{Na}_2\text{SO}_3$ ) accumulated in the waste water stream, are soluble and can be further oxidized to reduce the COD in the waste stream to the level acceptable to the municipal wastewater treatment plant. In contrast, the products calcium sulfite ( $\text{CaSO}_3$ ) or calcium sulfate ( $\text{CaSO}_4$ , aka gypsum) of the reaction between  $\text{SO}_2$  and calcium based agents are insoluble salts which are not easily removed from the scrubber solution.

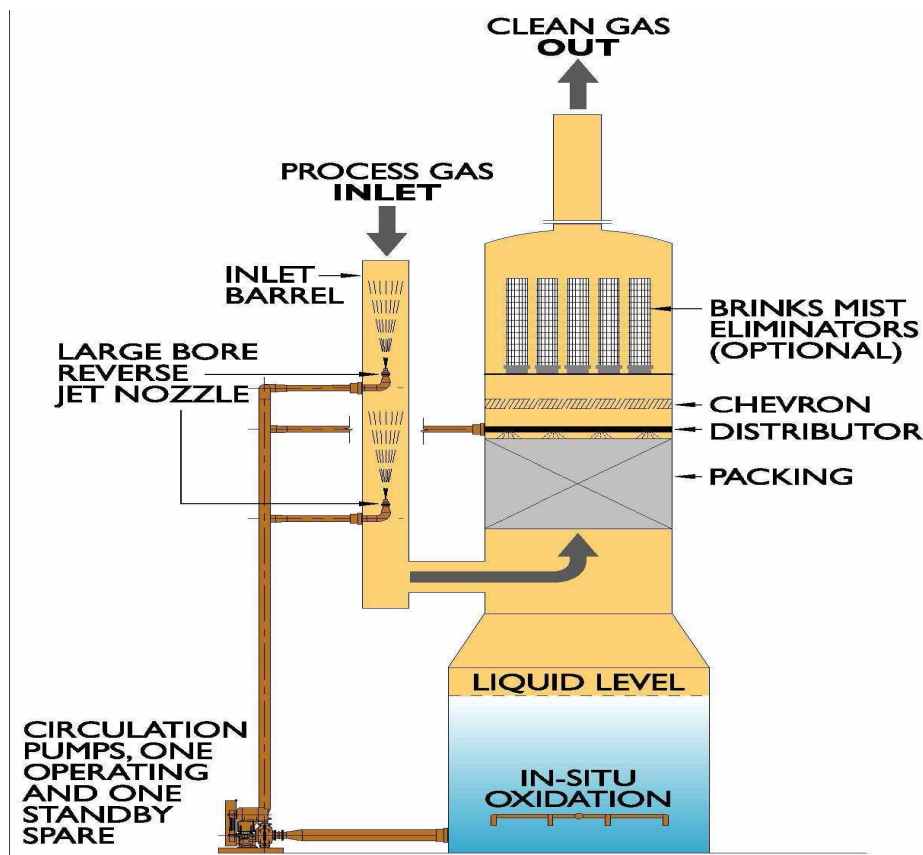
Using caustic solution as a scrubbing agent has helped the refineries to save on capital costs and annual operating costs, and improve the removal efficiency and operability of the system.-

Most DynaWave scrubbers contain two stages of scrubbing, or froth zones, in the inlet barrel, as shown in Figure 5-4. In the first scrubbing stage, the inlet process gas is adiabatically saturated or "quenched". The gas exits the first scrubbing stage at 150 – 180 degree F and passes through the second scrubbing stage. In the second stage, caustic liquid agent is again injected upward into the incoming gas. The  $\text{SO}_2$  is absorbed, and reacts with the caustic agent, forming sodium by products, sodium sulfite and sodium bisulfite salts.

The reverse jet nozzles, located in the inlet barrel and used to inject the caustic reagent, is a proprietary piece of equipment supplied by Monsanto Enviro-Chem System (MECS) which is very critical to the scrubber application. A relatively large volume of scrubbing liquid is injected counter to the gas flow to create a froth zone. The gas collides with the liquid, forcing the liquid toward the wall. A standing wave, created at the point the liquid is reversed by the gas, is an extremely turbulent region. In this turbulent region, the gas absorption and particulate collection is enhanced significantly.

If the SO<sub>2</sub> concentration in the inlet gas stream is high, Dynaware will include a third stage scrubbing consisting of 2-inch diameter metal packing rings added to further increase the gas/liquid absorption. The liquid agent circulated to the third stage scrubbing can be turned off when it is not needed.

**FIGURE 5-4**  
**DynaWave Wet Gas Scrubber Used for Sulfur Recovery Tail Gas Treatment Unit**



After passing through the third scrubbing stage, the air stream will pass through a set of chevrons which are used to maximize the liquid droplet removal. Liquid droplets disengage from the gas stream and accumulate in the bottom of the vessel. The bottom of the vessel is also used as a reservoir for the scrubber solution which ensure continuous feed to the recirculation pumps. Sulfite salts are also oxidized to sulfates in the reservoir. In addition to DynaWave scrubber, particulate filters, ESPs, or mist eliminators can be used downstream of the wet scrubber to remove fine particulates.

The Sinclair and Casper refineries have successfully operated the DynaWave scrubbers since 2004. Results of a full scale testing at Sinclair refinery in November 2005 are shown in Table 5-4. The system was proven to be 99.99% in sulfur removal efficiency and resulted in a SO<sub>2</sub>

outlet concentrations below 0.5 ppmv. In January 2005, Sinclair Oil Corporation decided to install a third DynaWave scrubber at its Tula refinery which has already started up in 2006.

**TABLE 5-4**  
**Full-Scale Performance of DynaWave Non-regenerative Scrubber**  
**for Sulfur Recovery Unit at Sinclair Refinery**

	Run 1	Run 2	Run 3	Average
SO <sub>2</sub> inlet, lbs/hr	276.10	259.13	249.50	261.58
SO <sub>2</sub> outlet, lbs/hr	0.01	0.01	0.01	0.01
SO <sub>2</sub> outlet, ppmv	0.31	0.31	0.31	0.31
SO <sub>2</sub> , % Removal	99.99	99.99	99.99	99.99

Note: Based on EPA Source Test Method 6. The 0.31 ppmv is the lowest detection level for stack testing. From *Improving Sulfur Recovery Units*, E. Juno of Sinclair Oil Corporation, S.F. Myer and C. Kulczycki of MECS, and N. Watts of CEntry Constructors and Engineers, Petroleum Technical Quarterly, Quarter 3 of 2006.

### 5.3.3.2 Cansolv<sup>®</sup> Regenerative Scrubber

Development of the Cansolv technology started in 1988 and begun by Union Carbide Canada Ltd.. Since then, it has been used commercially to control SO<sub>2</sub> from sulfur recovery units, sulfuric acid plants, cogeneration units, and power plant boilers. In California, the Cansolv technology has also been used to control SO<sub>x</sub> emitted from a sulfuric acid plant at an oil refinery since September 2002. The Cansolv scrubber also has been installed and operated since July 2006 to control SO<sub>x</sub> from a sulfur recovery - tail gas application at BP Cherry Point refinery. The project was developed by Marsulex Inc. and is subject to an annual mass limit of 135 tons per year which can be translated to 150 ppmv SO<sub>x</sub>.<sup>23</sup> Cansolv advertises that their regenerative scrubber can be designed ~~and was claimed~~ to achieve 10 ppmv SO<sub>2</sub>.<sup>24, 25, 26</sup>

<sup>23</sup> According to the 2<sup>nd</sup> Round of Comments on RECLAIM SO<sub>x</sub> Shave Staff Report Part I, dated July 1, 2008, the unit is designed to meet less than 200 ppmv, 12-hour rolling average, which is the limit of NSPA Subpart J/Ja. The unit has a mass limit of 135 tons per year, which can be translated to 150 ppmv SO<sub>x</sub>. The system was started in July 2006, was in operation for about 4 months, was shutdown due to equipment problems outside of the Cansolv system, and is currently not in operation.

<sup>24</sup> Hydrocarbon Engineering Word Review, 2007. [www.worldcoal.com/Hydrocarbon/HE\\_world\\_review\\_usa.htm](http://www.worldcoal.com/Hydrocarbon/HE_world_review_usa.htm)

<sup>25</sup> *Integrating Cansolv<sup>®</sup> System Technology into the Sour Gas Treating/Sulfur Recovery Plant* which indicated that Cansolv system can be designed to achieve 10 ppmv SO<sub>2</sub>. [www.cansolv.com](http://www.cansolv.com).

<sup>26</sup> *The Cansolv system process: A new paradigm for SO<sub>2</sub> recover and recycle*. J.N. Sarlis and P.M. Ravary of Cansolv Technologies, Inc.

## 5.4 Proposed BARCT Level and Emission Reductions

### 5.4.1 Performance of Units Located Within the SCAQMD Boundary

The existing performance levels of the sulfur recovery units in the District reported by the facilities through the 2008 Survey are listed in Table 5-5. The SO<sub>x</sub> concentrations at the stack of the thermal oxidizers vary widely from 17 ppmv – 150 ppmv.

**TABLE 5-5**  
**Performance of SRU-Tail Gas Treatment in SCAQMD**

Facility	% Sulfur Recovery	SO <sub>x</sub> Level
A	99.9%-99.99%	59 ppmv – 77 ppmv from thermal oxidizer
B	90%	98 ppmv – 150 ppmv from thermal oxidizer
C	---	17 ppmv – 56 ppmv from thermal oxidizer
D	99.9%	26 ppmv from thermal oxidizer
E	96%	20 ppmv from thermal oxidizer
F	99.5%	98 ppmv from thermal oxidizer
		<3 ppmv H <sub>2</sub> S outlet of tail gas treatment unit

### 5.4.3 Existing Performance for Units Located Outside of the SCAQMD

The performance of several recent sulfur recovery units operated by the refineries located outside of the SCAQMD are shown in Table 5-6. The units were designed to meet 99%-99.9% sulfur recovery efficiency.

**TABLE 5-6**  
**Performance of Sulfur Recovery – Tail Gas Treatment Unit**

Company	Source	SO <sub>x</sub> Standard
Arizona Clean Fuels Yuma LLC, Yuma AZ <sup>(1)</sup>	SRU - Tail Gas (Amine) Unit - Sour Water Stripper	99.97% sulfur recovery efficiency
BP, Texas City, Texas <sup>(2)</sup>	SRU	99% sulfur recovery. All refinery fuel gas is scrubbed to remove sulfur. Significant reductions by routing vent streams from the SRU to the front end of the SRU, to recover additional sulfur instead of combusting sulfur to SO <sub>2</sub> .
Shell Martinez, Contra Costa County, Bay Area <sup>(3)</sup>	SRU SCOT and tail gas thermal oxidizer	Limit at 50 ppmv at 0% O <sub>2</sub> . Test showed 13 ppmv SO <sub>2</sub> and <0.1 ppmv H <sub>2</sub> S at 0% O <sub>2</sub> .
Marathon Petroleum Garyville Refinery, Louisiana <sup>(1)</sup>	SRU with thermal oxidizers and oxygen enrichment	93 ppmvd SO <sub>2</sub> at 0% excess air, 99.9% sulfur recovery, 99.5% thermal oxidizer efficiency

Note: 1) The U.S. Environmental Protection Agency RACT/BACT/LAER Clearinghouse; 2) *BP Texas City Site – Texas City, Texas – 2004 Environmental Statement*, June 2005; 3) CARB BACT Clearinghouse.

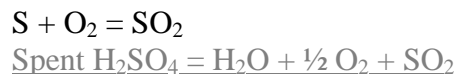
#### **5.4.4 Proposed BARCT Level and Emission Reductions**

As reported by the refineries in the District, the SRUs, tail gas treatment, and thermal oxidizers at Facility A and D can meet 99.9% - 99.99% sulfur recovery. Those at Facility C and E can meet less than or equal to 20 ppmv SO<sub>x</sub> at the stack of the thermal oxidizers, and Facility F can meet 3 ppmv H<sub>2</sub>S outlet of the tail gas treatment unit with current sulfur recovery technologies. In addition, wet gas scrubbers installed at refineries located outside of the Basin such as Dynawave at Sinclair refinery or Cansolv at BP Cherry Point refinery can meet less than or equal to 10 ppmv SO<sub>x</sub>. Combination of these technologies can help to reduce SO<sub>x</sub> emissions further. Staff will continue to conduct the BARCT analysis, estimate emission reductions and cost effectiveness, and report the findings in ~~p~~Part II and Part III of the ~~Preliminary~~ Draft Staff Report.

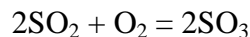
## Chapter 6 - Sulfuric Acid Manufacturing Process

### 6.1 Process Description

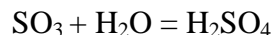
Sulfuric acid manufacturing process, as shown in Figure 6-1, includes three basic operations. First, ~~the~~ sulfur in the feedstock is oxidized and spent sulfuric acid is decomposed to sulfur dioxide (SO<sub>2</sub>) in a furnace:



The sulfur dioxide is then catalytically oxidized to sulfur trioxide (SO<sub>3</sub>) in a multi-staged catalytic reactor (or converter). A typical catalyst used in the reactor is vanadium:

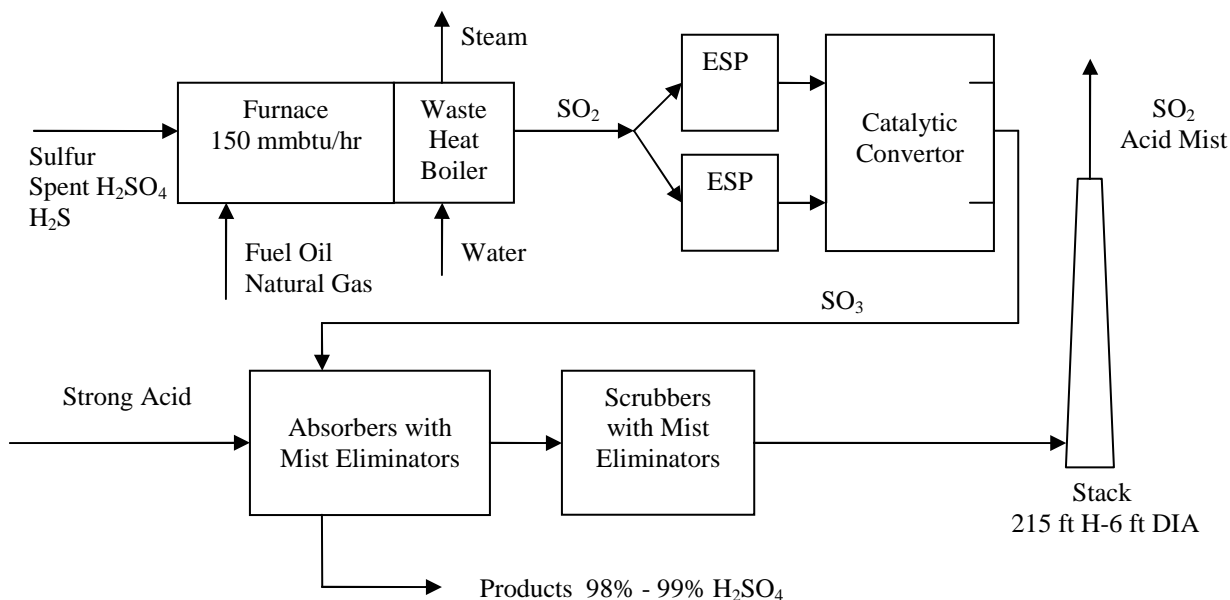


The sulfur trioxide ~~is absorbed~~ reacts with water in a absorbing tower to produce a strong sulfuric acid solution.



In a ~~and~~ double absorption process, the SO<sub>3</sub> gas formed from the primary converter is sent to a first absorber where ~~most of~~ the SO<sub>3</sub> is removed to form H<sub>2</sub>SO<sub>4</sub>. The remaining unconverted SO<sub>2</sub> and SO<sub>3</sub> are directed to a second set of converter and absorber to further ~~remove~~ produce H<sub>2</sub>SO<sub>4</sub>.

**FIGURE 6-1**  
**Sulfuric Acid Manufacturing Process**



The conversion to H<sub>2</sub>SO<sub>4</sub> is always incomplete, and is affected by the number of stages in the catalytic converter, the type and amount of catalyst used, temperature and pressure, and the concentrations of the reactants, SO<sub>2</sub> and O<sub>2</sub>. A 98% - 99% conversion to H<sub>2</sub>SO<sub>4</sub> is typical. The exhaust gas stream from the absorbers can be vented to ESPs, scrubbers, and mist eliminators to remove SO<sub>2</sub> and acid mist prior to venting to the atmosphere. The process produces a great deal of heat. Steam driven compressors, waste heat boilers, and heat exchangers are utilized throughout the process to recover and convert the waste heat into useful energy.

## 6.2 Current Allocations and Emissions

### 6.2.1 Allocations

Facility A and B are the two facilities in the District that operate a sulfuric acid manufacturing plants. In 1993, allocations were provided to these processes based on an emission factor ranging from 4 lbs/ton acid produced to 9.478 lbs/ton acid produced. The existing SCAQMD Rule 409469 limits the SO<sub>2</sub> concentration in effluent process gas from a sulfuric acid unit to 500 ppmv and the mass emissions to 198.5 lbs/hr of sulfur compounds expressed as SO<sub>2</sub>; and NSPS requires a sulfuric acid manufacturing plant to meet an emission level of 4 lb SO<sub>2</sub> per ton of 100% acid produced, maximum 2 hour average. The allocations provided to these two facilities are shown in Table 6-1.

**TABLE 6-1**  
**Allocations for Sulfuric Acid Furnace/Reactor**

Facility	Peak Year	Emission Factor (lbs per ton acid produced)	Allocations (lbs/year)	Allocations (tons/day)
A	1988	4.000	598,028	0.82
B (Plant 1)	1987	4.380	371,139	0.51
B (Plant 2)	1987	4.577	329,031	0.45
B (Plant 3)	1989	9.478	549,904	0.75
			<b>Total</b>	<b>2.53</b>

Note: Prior to 1990, Facility B operated three sulfuric acid units that were built between the late 1920's and late 1950's. In 1990, these three furnaces were replaced with a double absorption furnace to achieve 99.85% conversion efficiency and currently subject to EPA Consent Decree limiting the emission rate to 1.7 lbs SO<sub>2</sub> per ton of acid produced.

In addition to SO<sub>2</sub>, there is acid mist generated from the absorber of the sulfuric acid manufacturing process. Acid mist is generated when SO<sub>3</sub> combines with water at temperature below the dew point of SO<sub>3</sub>. Acid mist is a very stable compound and usually is controlled and captured by mist eliminators. Sulfuric acid mist is limited to 0.15 lbs per ton acid produced under NSPS and 0.30 lbs per ton acid produced under SCAQMD Rule 469.

### 6.2.1.2 Emissions

The 2005 emissions reported from these processes are presented in Table 6-2. The furnace at Facility B reported emitted 1.13 tons per day and the sulfuric acid reactor at Facility A reported 0.04 tons per day. At 1.13 tons per day, Facility B's furnace is the top #1 emitter in the District in 2005.

The two facilities also reported their 2006 and 2007 emissions ~~from their furnaces~~ through the SCAQMD Survey conducted in 2008, as shown in Table 6-2. The production rate of 100% sulfuric acid at Facility B is approximately 3 times larger than the production rate at Facility A.

**TABLE 6-2**  
**SO<sub>2</sub> Emissions from Sulfuric Acid Furnace/Reactor**

Facility	Device Description	2005 Emissions (tons/day)	2006 Emissions (tons/day)	2007 Emissions (tons/day)
A	Reactor	0.04 <sup>(1)</sup>	0.06	0.05
B	Furnace	1.13 <sup>(2)</sup>	1.02	0.96
		<b>1.167</b>	<b>1.08</b>	<b>1.01</b>

Note: 1) The emissions are ~~from a single absorption unit and vented to~~ controlled by a Cansolv scrubber, 2) The emissions are ~~vented to a venture scrubber, a packed bed scrubber, a mist eliminator, and a flare~~ from a double absorption unit.

The emissions from Facility A's reactor are low compared to the emissions from Facility B's furnace. Facility A's single absorption unit uses a Cansolv scrubber to control their SO<sub>x</sub> emissions from the reactor, whereas the emission from Facility B's ~~furnace~~ double absorption unit ~~are~~ is currently not controlled by scrubbers ~~vented to a series of control devices including a venturi scrubber from Environmental Systems Technology, a packed bed scrubber from Environmental Systems Technology, a mist eliminator, and a flare.~~ The SO<sub>x</sub> outlet concentrations from Facility B's furnace were in a range of ~~100~~144 ppmv – ~~190~~185 ppmv, whereas the SO<sub>x</sub> outlet concentrations from Facility A's reactor were in a range of 17 ppmv – 51 ppmv. The emission rates calculated based on the information reported through the 2008 Survey are from 1.58 lbs/ton – 1.84 lbs/ton acid produced for Facility B, and 0.28 lbs/ton acid for Facility A. ~~It should be noted that Facility B's furnace is the top #1 SO<sub>x</sub> emitter in the District in 2005 at 1.13 tons per day.~~

## 6.3 Control Technology

### 6.3.1 EPA BARCT Clearinghouse

Staff researched the U.S. EPA RACT/BACT/LAER Clearinghouse to identify the BARCT level for sulfuric acid manufacturing plant. A summary of the information— posted on the Clearinghouse is presented in Table 6-3. ~~Staff is in the process of verifying these information with the U.S. EPA to find out whether the limit of 0.2 lbs SO<sub>x</sub> per ton acid is applicable for new or retrofitted equipment.~~<sup>27</sup>

In general, in addition to double absorption, the sulfuric acid manufacturing plants in the U.S. have upgraded their converters and absorbers,– used cesium promoted vanadium catalysts, and added tail gas scrubbers to meet an emission level ranging from 0.2 lbs – 3.5 lbs SO<sub>x</sub> per ton of 100% acid produced.

<sup>27</sup> U.S. EPA RACT/ EPA RACT/BACT/LAER Clearinghouse.



**TABLE 6-3**  
**Emission Levels for Sulfuric Acid Manufacturing Plants <sup>(1)</sup>**

<b>Facility</b>	<b>Source</b>	<b>SOx Level</b>
Dupont, Union, New Jersey ( <a href="#">New Construction in 2007</a> )	Two identical 400 tons per day double absorption sulfuric acid plants that use spent acid, sulfur, and hydrogen sulfide as feed stocks.	<ul style="list-style-type: none"> <li>– 0.2 lbs SOx per ton of 100% acid produced and 3 lbs/hr SOx at 3-hour average<sup>(2)</sup></li> <li>– 0.10 lbs sulfuric acid mist per ton of 100% acid produced.</li> </ul>
Dupont, El Paso, Texas ( <a href="#">New Construction in 2007</a> )	Double absorption sulfuric acid plant that use spent acid and hydrogen sulfide as feed stocks.	<ul style="list-style-type: none"> <li>– 1 lbs SOx per ton of 100% acid produced at 3-hour average</li> <li>– 0.10 lbs sulfuric acid mist per ton of 100% acid produced.</li> </ul>
Dupont, New Castle, DE ( <a href="#">New Construction in 2005</a> )	Double absorption sulfuric acid plant, 550 tons per day, that use spent acid and hydrogen sulfide as feed stocks.	<ul style="list-style-type: none"> <li>– 1.35 lbs SOx per ton of 100% acid produced at 3-hour average</li> <li>– 0.12 lbs sulfuric acid mist per ton of 100% acid produced.</li> </ul>
General Chemical LLC, Augusta, Richmond	Double absorption sulfuric acid plant, 1,000 tons per day. A new soda ash scrubber was used to lower the standard from 4 lbs to 2.6 lbs/ton	<ul style="list-style-type: none"> <li>– 2.6 lbs SOx per ton of 100% acid produced at 3-hour average</li> <li>– 0.08 lbs sulfuric acid mist per ton of 100% acid produced.</li> </ul>
CF Industries, Hillsborough, Florida	Double absorption plant, 1,600 tons/day, uses spent acid, sulfur, and hydrogen sulfide as feed stocks. This plant has a two-stage ammonia scrubber and upgraded converters. The plant uses cesium catalysts to increase the SO <sub>2</sub> -SO <sub>3</sub> conversion.	<ul style="list-style-type: none"> <li>– 3.5 lbs SOx per ton of 100% acid produced, 99.5% conversion, and 401 lbs/hr SOx at 3-hour avg.</li> <li>– 0.10 lbs sulfuric acid mist per ton of 100% acid produced, 99% control efficiency, and 11 lbs/hr sulfuric acid mist.</li> </ul>
CF Industries, Plant City, Florida	Two 2,750 tons per day double absorption plants that use spent acid, sulfur, and hydrogen sulfide as feed stocks. The converters and absorbers were upgraded and cesium promoted vanadium catalysts were used to increase the SO <sub>2</sub> -SO <sub>3</sub> conversion.	<ul style="list-style-type: none"> <li>– 3.5 lbs SOx per ton of 100% acid produced, 99.5% conversion, and 401 lbs/hr SOx at 3-hour average</li> <li>– 0.10 lbs sulfuric acid mist per ton of 100% acid produced, 99% control efficiency, and 11 lbs/hr sulfuric acid mist.</li> </ul>
US Agri-Chemicals Corp., Polk, Florida	A 3,000 tons per day double absorption sulfuric acid plant with mist eliminators	<ul style="list-style-type: none"> <li>– A 3.5 lbs SOx per ton 100% acid produced, and 99.9% conversion efficiency, and 1916 tons per year</li> <li>– 0.12 lbs sulfuric acid mist per ton of 100% acid produced, 99% control efficiency, and 65.7 tons per year sulfuric acid mist.</li> </ul>

Note: 1) EPA RACT/BACT/LAER Clearinghouse on EPA's web page conducted in November 2007. 2) Staff is in the process of verifying with the U.S. EPA to whether or not the limit of 0.2 lbs/ton is applicable for new or retrofit equipment.

### 6.3.2 Clean Air Act Settlements

Recently in 2007, the U.S. Department of Justice and the U.S. EPA have announced several Clean Air Act settlements with two major sulfuric acid plants in the country to lower the SO<sub>2</sub> emissions from their sulfuric acid plants in the country.

- Company #1 operates four sulfuric acid plants in Louisiana, Virginia, Ohio, and Kentucky. Under the recent settlements, the company has agreed to install a \$66 million state-of-the-art dual absorption control equipment in its largest plant located in Darrow, Louisiana. For the other three plants, the company has the option to install the \$87 million additional control technologies or ceasing operations. All four plants have to meet the lower standards ranging from 1.7 lbs – 2.4 lbs SO<sub>2</sub> per ton acid produced by March 1, 2012. When fully implemented, these plants will reduce SO<sub>x</sub> by an additional 90%. A summary of these agreements is included in Table 6-4.<sup>28</sup>
- Company #2 has agreed to spend approximately \$50 million to upgrade air pollution control at their eight production plants in four states across the country to reduce SO<sub>2</sub> emissions by approximately 95%. As shown in Table 6-4, the consent decree requires the installation of wet gas scrubbers or double absorption technology to meet the BARCT levels ranging from 1.7 lbs – 2.5 lbs SO<sub>x</sub> per ton acid produced.<sup>29</sup>

**TABLE 6-4**  
**Consent Decree for Sulfuric Acid Manufacturing Plants**

Company	SO <sub>x</sub> Level (lbs SO <sub>2</sub> per ton)	Compliance Date
#1, Burnside, Darrow, Louisiana	2.4 <sup>(1)</sup>	September 1, 2009
#1, James River, Richmond, Virginia	1.5 <sup>(1)</sup>	March 1, 2010
#1, Fort Hill, North Bend, Ohio	2.2 <sup>(1)</sup>	March 1, 2012
#1, Wurtland, Wurtland, Kentucky	1.7 <sup>(1)</sup>	March 1, 2012
#2, Hammond, Indiana <sup>(3)</sup>	2.5 <sup>(2)</sup>	Not specified
#2, Martinez, California <sup>(4)</sup>	2.2 <sup>(2)</sup>	Not specified
#2, Dominguez, California <sup>(3)</sup>	1.7 <sup>(2)</sup>	Not specified
#2, Bayton, Texas <sup>(4)</sup>	2.2 <sup>(2)</sup>	Not specified
#2, Houston #8, Texas <sup>(5)</sup>	1.7 <sup>(2)</sup>	Not specified
#2, Houston #2, Texas <sup>(5)</sup>	1.8 <sup>(2)</sup>	Not specified
#2, Baton Rouge #2, Louisiana <sup>(5)</sup>	2.2 <sup>(2)</sup>	Not specified
#2, Baton Rouge #1 Louisiana <sup>(5)</sup>	1.9 <sup>(2)</sup>	Not specified

Note: 1) the standard is a 3-hour rolling average. 2) The standard is a 365-day rolling average. Company #2 plants must meet 0.15 lbs/ton acid mist. 3) Double absorption plant. 4) Single absorption with ammonia scrubber. 5) Single absorption with caustic scrubber.

## 6.4 Proposed BARCT Level and Emission Reductions

As shown in Tables 6-3 and 6-4, the controlled emission level for sulfuric acid manufacturing plants has been improved significantly. The current controlled level can be as low as 0.2 lbs/ton – 0.3 lbs/ton. These levels could be achieved by upgrading the converters and absorbers, using cesium promoted vanadium catalysts, and/or adding tail gas scrubbers.

<sup>28</sup> Civil Clean Air Act Settlements. [www.usdoj.gov](http://www.usdoj.gov)

<sup>29</sup> Civil Clean Air Act Settlement, [www.uepa.gov/compliance/resources/cases/civil/caa/rhodia-fcsht.html](http://www.uepa.gov/compliance/resources/cases/civil/caa/rhodia-fcsht.html)

In the District, Facility A has used Cansolv scrubber to control SOx emissions from its acid production plant, and achieved 0.28 lbs/ton acid produced. As a result, the emissions from its reactor ~~has~~have dropped from 0.82 tons per day in 1993 to 0.04 tons per day in 2005. By using Cansolv scrubber, Facility A has achieved an emission reduction of approximately  $(1 - 0.04/0.82) * 100 = 95\%$ .

The emissions from Facility B's furnace are currently not vented to ~~a series of scrubbers, designed to be at 99.9% efficiency.~~<sup>30</sup> Nevertheless, ~~the~~The SOx emissions from this facility's furnace were ~~still in~~ a range of ~~100~~144 ppmv – ~~190~~185 ppmv, and this furnace ~~is~~was still the #1 SOx emitter in the District at 1.13 tons per day in 2005.

~~Staff will continue to research. In order to assess an appropriate BARCT level for sulfuric acid plant, staff released a Request for Proposal in July 2008 and contracted the feasibility and costs analysis to NEXIDEA, Inc. in September 2008. NEXIDEA's technical report is summarized in Part II of the Draft Staff Report, determine the potential emission reductions and cost effectiveness, and report the findings in Part II of the Preliminary Draft Staff Report.~~

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<sup>30</sup> Permit condition no A72.1 in Facility B's Facility Permit, dated September 2007. The 99.9% efficiency seems not correlated well with the SOx outlet concentrations recorded in the range of 144 – 185 ppmv from the furnace.

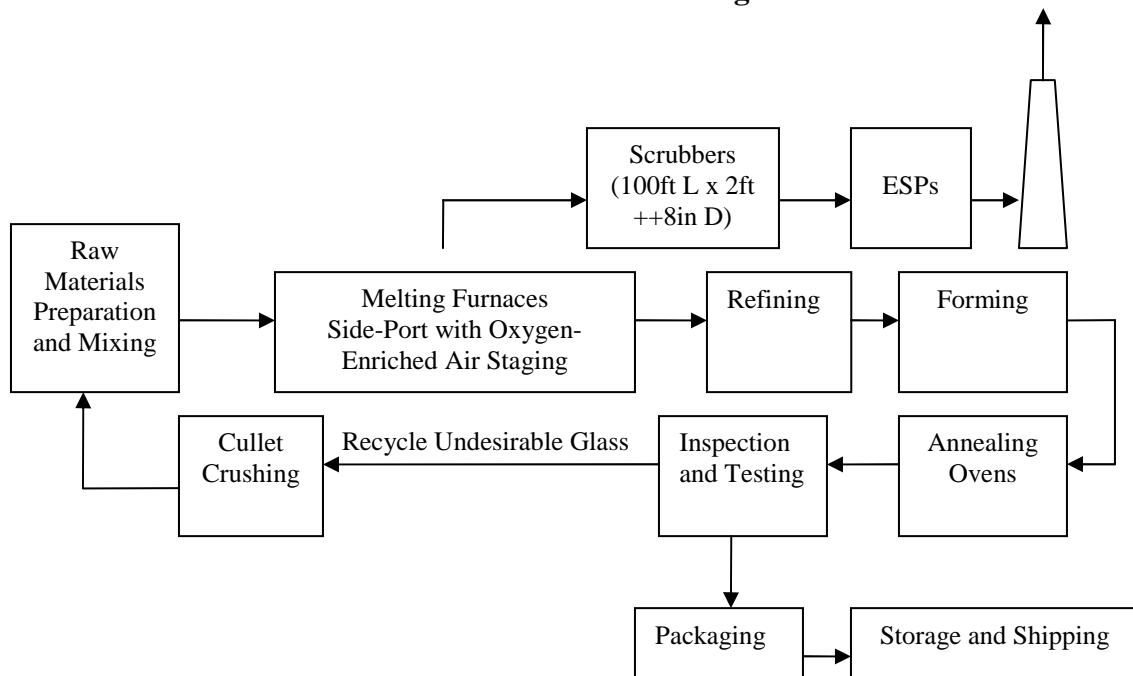
# Chapter 7 - Container Glass Manufacturing Process

## 7.1 Process Description

Owens-Brockway Glass Container Inc. is a container glass manufacturing facility located in Vernon. The company manufactures glass bottles, glass wares, pressed & blown glass, tempered glass, as well as safety glass. The manufacturing process contains four phases 1) preparation of raw material, 2) melting in a furnace, 3) forming, and 4) finishing. Figure 7-1 is a simplified diagram for a typical glass manufacturing process.

Raw materials, which include sand, limestone, and soda ash, are crushed and mixed with cullets to ensure homogeneous melting. The raw materials are then conveyed to a continuous regenerative side-port melting furnace. As the materials enter the melting furnace through a feeder, they float on the top of the molten glass already in the furnace, melt, and eventually flow to a refiner section, and then fore hearths, forming machine, and annealing ovens. The final products undergo inspection, testing, packaging and storage. Any damaged or undesirable glass is transferred back to be used as cullets.

**FIGURE 7-1**  
**Container Glass Manufacturing Process**



Sulfur oxides are generated from the decomposition of the sulfates in the raw materials and sulfur in the fuel. The melting furnace contributes over 99% of the total emissions from a glass plant. There are currently two melting furnaces at the Vernon facility, a 60 mmbtu/hr furnace #23B (Device D147), and a 100 mmbtu/hr furnace #23C (Device ID D112). Each furnace is limited to approximately 400 tons glass pulled per day. The SO<sub>x</sub> emissions are controlled by two scrubbers, of which one scrubber has a permit condition of 80% efficiency. The scrubbers are manufactured by PPC Industries, use sodium bi/sesquicarbonate as scrubbing agent, have two passes, and about 101 ft in length and 2ft 8 in diameter. The outlet flue gases from the scrubbers are directed to a common manifold and are vented to three dry ESPs downstream, one standby, for particulate emissions control. The furnaces currently have oxygen-enriched air staging (oxy-fuel), a control technique that is commonly used to reduce NO<sub>x</sub>.

## 7.2 Current Allocations and Emissions

### 7.2.1 Allocations

The allocations provided to the facility for their furnaces are presented in Table 7-1. These allocations were estimated based on SO<sub>x</sub> emission factors ranging from 2.12 lbs/ton to 3.15 lbs/ton of glass pulled, and their peak activities in 1992. The total allocations provided for the three furnaces was 1.01 tons per day.

**TABLE 7-1**  
**Allocations for Container Glass Melting Furnaces**

<b>Equipment</b>	<b>Peak Year</b>	<b>Emission Factor (lbs per ton glass)</b>	<b>Allocations (lbs/year)</b>	<b>Allocations (tons/day)</b>
Furnace #1	1992	3.150	231,475	0.32
Furnace #2	1992	2.480	269,673	0.37
Furnace #3	1992	2.120	237,605	0.33
			<b>Total</b>	<b>1.01</b>

### 7.2.2 Emissions

The emissions reported in 2005, 2006 and 2007 from Owens-Brockway's furnaces are presented in Table 7-2. In total, the two furnaces emitted about 0.21 tons per day SO<sub>x</sub> in 2005, 0.27 tons per day in 2006, and 0.35 tons per day in 2007. The emissions from the two furnaces were vented to two scrubbers (one scrubber dedicated to each furnace); and three parallel ESPs (shared between two furnaces). The emissions were measured by three CEMS. The SO<sub>x</sub> outlet concentrations were averaged 64 ppmv for the first CEMS, 69 ppmv for the second CEMS, and 85 ppmv for the third CEMS. In addition to Owens-Brockway, Saint-Gobains Containers Inc. operated a 78 mmbtu/hr glass melting furnace that emitted about 0.13 tons per day SO<sub>x</sub> in 2005, but this operation has ceased since then.

**TABLE 7-2**  
**SOx Emissions from Glass Melting Furnaces**

<b>Facility</b>	<b>SOx Avg Concentration (ppmv)</b>	<b>2005 Emissions (tons/day)</b>	<b>2006 Emissions (tons/day)</b>	<b>2007 Emissions (tons/day)</b>
Owens-Brockway, A CEMS	64	0.076	0.27	0.35
Owens-Brockway, B CEMS	69	0.084		
Owens-Brockway, C CEMS	85	0.036		
Saint-Gobain (shutdown)	NA	0.128	NA	NA
		<b>0.32</b>	<b>0.27</b>	<b>0.35</b>

Note: The 2005 SOx emissions were from SCAQMD database for the period from January 2005 – December 2005. The 2006 and 2007 emissions were reported by the facilities through a Survey Questionnaire distributed by SCAQMD in 2008.

Through the 2008 Survey, Owens-Brockway reported that the two furnaces were in operating at > 90% maximum rated capacity from 2005-2007 and have emission rates ranging from 0.62 lbs/ton – 1.05 lbs/ton glass pulled, as shown in Table 7-3.

**TABLE 7-3**  
**SOx Emission Rates from Glass Melting Furnaces**

<b>Year</b>	<b>SOx Emission Rates (Lbs/Ton of Glass Pulled)</b>
2005	0.62
2006	0.80
2007	1.05

### 7.3 Control Technology

In 2005, the U.S. Department of Justice and the U.S. EPA have reached an agreement with Saint-Gobain Containers, Inc. and required Saint-Gobain to install state-of-the-art pollution control at a cost of \$6.6 million to reduce SO<sub>2</sub> emissions from their melting furnaces. The Saint-Gobain plant located in Seattle Washington was permitted to a level of 1.6 lbs SO<sub>x</sub> per ton glass produced with the use of Tri-Mer Cloud Chamber Scrubber (CCS).<sup>31</sup> The installation of the CCS was just recently finished, and the plant started testing in mid of December 2007. The capital costs for the CCS at this plant were approximately \$1,694,000, designed for an inlet flow of 40,000 acfm at 700 degree F.<sup>32</sup>

Other Saint-Gobain facilities must meet a level of 0.8 lbs SO<sub>2</sub> per ton of glass pulled. This 0.8 lbs/ton is the most recent BARCT level for container glass melting furnaces and has been

<sup>31</sup> Title V Permit & Statement of Basis for Saint-Gobain Containers Inc. located in Seattle prepared by the Puget Sound Clean Air Agency, dated June 6, 2007.

<sup>32</sup> E-mail from Mr. Gerry Pade of Pudget Sound Clean Air Agency to Minh Pham, dated November 30, 2007.

proposed by San Joaquin Valley APCD in their proposed rule 4354.<sup>33, 34</sup> Tri-Mer Corporation estimates that their technology can achieve a level as low as 0.1 lbs SO<sub>2</sub> per ton of glass produced, 0.1 ppmv outlet SO<sub>2</sub>, and 99.9% control efficiency. The BARCT information for glass melting furnaces is summarized in Table 7-3.

**TABLE 7-3**  
**BARCT for Container Glass Manufacturing Plant**

Facility	SO <sub>x</sub> Level
Saint-Gobain Containers, Inc., Seattle, Washington	1.6 lbs per ton glass produced <sup>(1, 2)</sup>
San Joaquin Valley APCD Proposed Rule 4354	0.8 lbs/ton glass produced
Tri-Mer Cloud Chamber Scrubber	0.1 ppmv SO <sub>2</sub> outlet 0.1 lbs per ton glass produced 99.9% control efficiency <sup>(3)</sup>

Note: 1) This is the permitted level of SO<sub>x</sub> from Saint-Gobain furnaces controlled by a Tri-Mer Cloud Chamber Scrubber which was designed to handle an exhaust flow of 40,000 acfm at 700 F. The furnaces are either operated at a) 205 tons per day capacity with an exhaust flow rate of 35,600 acfm at 350 F, or b) 195 tons per day capacity with an exhaust flow rate of 15,000 acfm at 500 F. 2) Fuel oil burning in these furnaces is limited to 15 ppmv by weight of sulfur (0.0015%). 3) Information provided by Tri-Mer Corporation based on their own source testing information.

## 7.4 Proposed BARCT Level and Emission Reductions

Given that Owens Brockway achieved a level of 0.62 lbs/ton in 2005, averaged 64 ppmv - 85 ppmv SO<sub>x</sub>, with the use of dry scrubbing, and Tri-Mer Cloud Chamber wet scrubbing can achieve 0.1 lbs/ton, 0.1 ppmv SO<sub>x</sub>, staff believes that further emission reductions from container glass manufacturing is feasible. Staff will continue to evaluate the potential BARCT level (e.g. ≤ 0.6 lbs/ton), emission reductions, cost effectiveness, and report the findings in Part II and Part III of the Preliminary Draft Staff Report.

<sup>33</sup> Consent Decree for Saint-Gobain Containers, Inc.

[www.epa.gov/compliance/resources/reports/endofyear/eoy2005/2005aircasehighlights.html](http://www.epa.gov/compliance/resources/reports/endofyear/eoy2005/2005aircasehighlights.html).

<sup>34</sup> San Joaquin Valley APCD Rule 4354 – Glass Melting Furnaces, Proposed Amended Rule and Draft Staff Report, dated February 8, 2008.

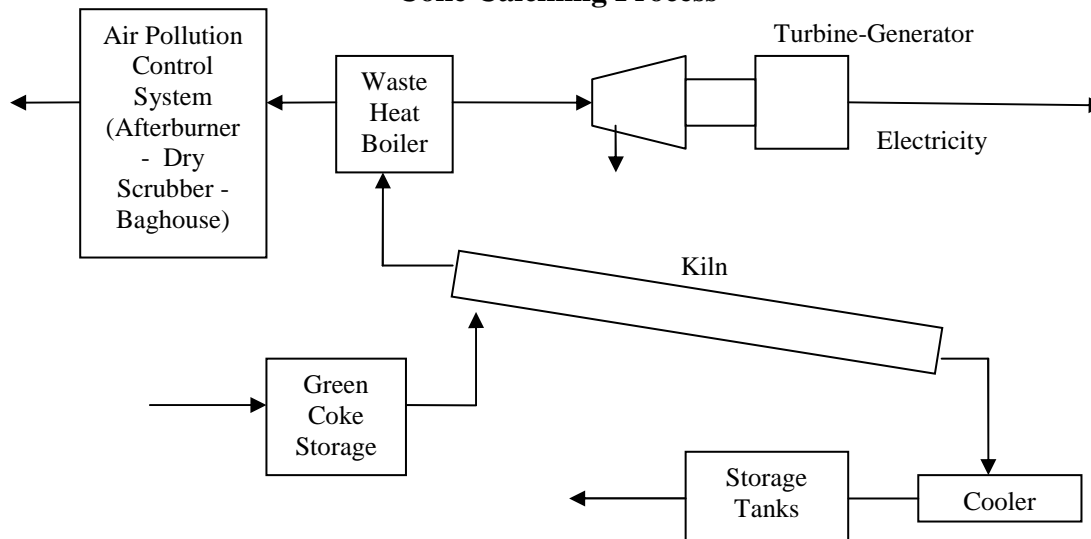
## Chapter 8 - Coke Calcining

### 8.1 Process Description

Engineering of the coke facility began in 1978 by Martin-Marietta. Initial production of calcined coke occurred in February 1983. The company was purchased by BP Products Company in 1985. BP produces calcined coke in two locations in the United States: Wilmington California and Cherry Point Washington, and two locations in Germany: Gelsenkirchen and Lingen.

Basically, coke calcining is a process to improve the quality and value of “green coke” produced at a delayed coker in a refinery. At BP Wilmington, the green feed, produced by BP’s nearby Carson Refinery, is screened and transported to the BP Wilmington Calciner by truck, where it is stored under cover in a coke storage barn. The screened and dried green coke is introduced into the high end of the rotary kiln, 3 feet diameter x 270 ft long, is tumbled by rotation, moves down the kiln countercurrent to a hot stream of combustion air produced by the combustion of natural gas or oil. The kiln temperatures are in a range of 2000 – 2500 degrees Fahrenheit. The green coke is retained in the kiln for approximately one hour to drive off the moisture, impurities, and hydrocarbon. After discharging from the kiln, the calcined coke drops into a cooling chamber, where it is quenched with water, treated with dedusting agents for dust control, carried by conveyors to storage tanks, and later are transported by trucks to the Port of Long Beach for export, or is loaded into railcars for shipments to domestic customers. A simplified process diagram of the calcining process is shown in Figure 8-1.

**FIGURE 8-1**  
**Coke Calcining Process**





BP Wilmington produces approximately 400,000 short tons per year of calcined products.<sup>35</sup> The Wilmington coke calciner is limited to a maximum processing rate of 1,980 tons green coke per day, and is increasing to 2,400 tons of green coke per day.<sup>36</sup> BP Wilmington is a global supplier of calcined coke to the aluminum industry, and fuel grade coke to the fuel, cement, steel, calciner, and specialty chemicals businesses.

## 8.2 Current Allocations and Emissions

### 8.2.1 Allocations

As shown in Table 8-1, the allocations for BP coke calciner was estimated based on a controlled emission factor of 2.473 lbs SOx per ton of calcined coke and a production rate of 378,264 tons calcined coke.<sup>37</sup> The coke calciner was in compliance with SCAQMD Rule 1119 – Petroleum Coke Calcining Operations – Oxides of Sulfur, adopted March 2, 1979, which requires that the uncontrolled SOx emissions from coke calcining operations must be reduced by at least 80% by July 1, 1983.

**TABLE 8-1**  
**Allocations for BP Coke Calciner**

<b>Peak Year</b>	<b>Emission Factor (lbs per ton coke)</b>	<b>Allocations (lbs/year)</b>	<b>Allocations (tons/day)</b>
1989	2.473	935,447	1.28
		<b>Total</b>	<b>1.28</b>

### 8.2.2 Emissions

The 2005-2007 reported emissions from BP coke calciner is presented in Table 8-2. Note that the 2005-2007 emissions are much less than the allocations provided to BP in 1993.

**TABLE 8-2**  
**SOx Emissions from BP Coke Calciner**

<b>Device ID</b>	<b>Rating (mmbtu/hr)</b>	<b>2005 Emissions (tons/day)</b>	<b>2006 Emissions (tons/day)</b>	<b>2007 Emissions (tons/day)</b>
20	120	0.35	0.62	0.55
<b>Total</b>		<b>0.35</b>	<b>0.62</b>	<b>0.55</b>

Note: The 2005 SOx emissions were from SCAQMD database for the period from January 2005 – December 2005. The 2006 and 2007 emissions were reported by the facilities through a Survey Questionnaire distributed by SCAQMD in 2008.

<sup>35</sup> BP Coke at Wilmington, <http://coke.bp.com/tech/tech.cfm>, September 2007.

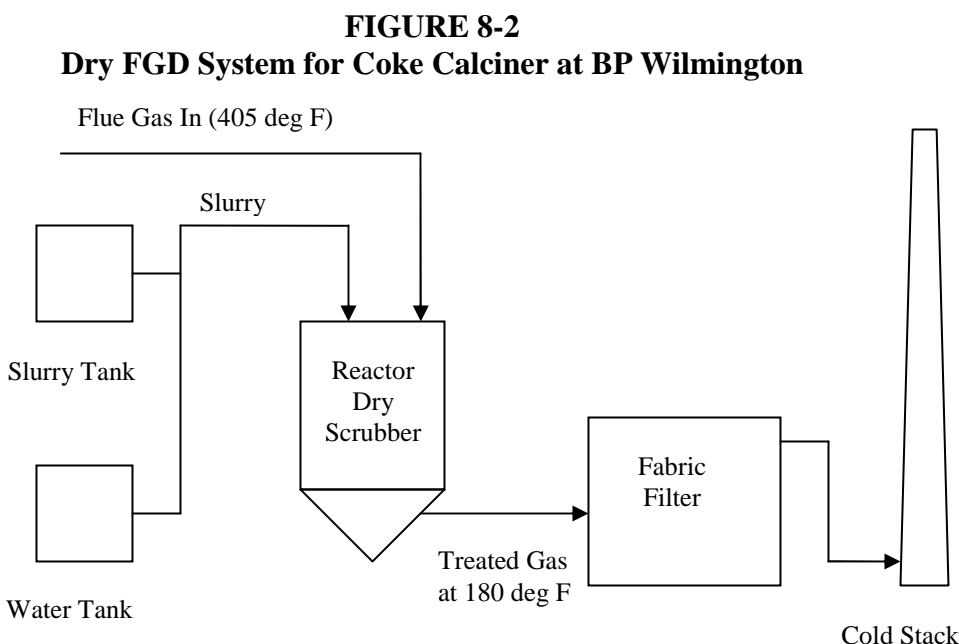
<sup>36</sup> SCAQMD Facility Permit to Operate of BP West Coast Products LLC, BP Wilmington, Draft, Version September 2007.

<sup>37</sup> SCAQMD Tier I Emission Rate, RECLAIM, 2002

## 8.3 Control Technology

### 8.3.1 Dry Scrubber at BP Wilmington

Dry scrubbing is the chosen control technology for the BP Wilmington coke calciner. The control system includes a spray dryer, a reverse-air baghouse, ~~a packaged limer slakin~~, a slurry storage system, a slurry circulating system, and a pneumatic conveying system. Calcium hydroxide (CaOH) slurry is the absorbing medium for SO<sub>2</sub> control. Figure 8-2 shows a simplified process diagram for the dry scrubber system at BP Wilmington..



The system was designed and guaranteed to achieve 90% control efficiency for SO<sub>x</sub> at a calcined coke capacity of 54 tons/hour (1,296 tons/day or 473,040 tons/year). The SO<sub>x</sub> emission rates were tested in July 1983 to provide verification of guarantees. Production rate during the tests averaged 50 tons per hour and the emission rates ranged from 0.21 lbs/ton – 1.64 lbs/ton, averaged at 1 lbs/ton coke.<sup>38</sup> It should be noted that the Tier I controlled emission level of SO<sub>x</sub> from the calciner provided in 1993 is 2.47 lbs/ton coke, even though the system was designed and tested to meet lower levels than 2.47 lbs/ton.

A recent source test conducted at BP Wilmington calciner kiln reported a level of approximately 66 ppmv SO<sub>x</sub> at a processing rate of 1,848 tons green coke per day. The processing rate was substantially higher than the processing rate used for the original design at 1,296 tons per day to achieve 90% efficient.<sup>39</sup>

<sup>38</sup> *Performance of Dry Flue Gas Desulfurization on a Petroleum Coke Kiln Application*, R.J. Horn of Ecolaire Environmental Company and J.F. Bent of Martin Marietta Aluminum, Journal of the Air Pollution Control Association, September 1984.

<sup>39</sup> SCAQMD Source Test Report, R01032.

In responding to the 2008 Survey, BP indicated that the performance of the dry scrubber in 2005-2007 exceeded the design levels. The control efficiencies for the dry scrubber in 2005-2007 were in a range of 98% - 99%. The averages of SO<sub>x</sub> outlet concentrations in 2005-2007 were in a range of 27 ppmv – 43 ppmv, with some RATA tests conducted in 2006 and 2007 showed a higher level at 82 ppmv at 4% O<sub>2</sub> and 84 ppmv at 5% O<sub>2</sub>. BP reported that with the dry scrubber, their emission rates in 2005-2007 were in a range of 0.56 – 0.89 lbs SO<sub>x</sub> per ton coke. Table 8-3 shows a comparison between design parameters and current performance in 2005-2007.

**TABLE 8-3**  
**Design Parameters and Current Performance of**  
**Dry Scrubber for BP Wilmington Coke Calciner**

	<b>Design Parameter</b>	<b>2005 Performance</b>	<b>2006 Performance</b>	<b>2007 Performance</b>
Processing Rate (tpd)	1,296			
Control Efficiency (%)	90%	99%	98%	99%
Emission Rate (lbs/ton)	0.21–1.64	0.56	0.97	0.89
SO <sub>x</sub> Concentration (ppmv)	Not Measured	27 ppmv	52 ppmv	43 ppmv

### 8.3.2 Wet Scrubber and Wet ESP at BP Cherry Point Refinery

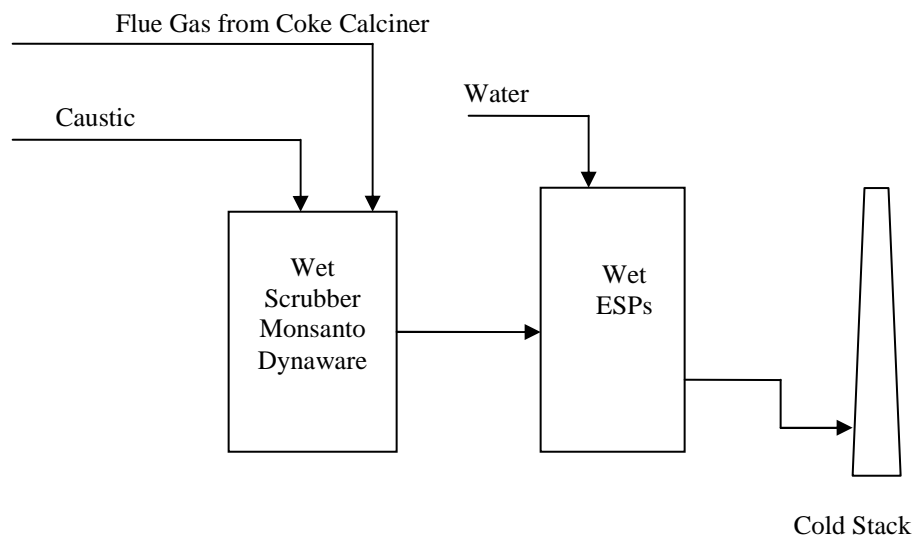
In addition to the coke calciner at Wilmington, BP operates three calciners at Cherry Point Refinery in Blaine, Washington. ~~In 1984~~Originally, BP voluntarily installed a wet scrubber to control SO<sub>x</sub>. ~~In 1994~~Later, the company removed a portion of the wet scrubber and installed a wet electrostatic precipitator (WESP) to further control sulfuric acid mist emissions from the calciners, as shown in Figure 8-3.

In ~~2001~~addition, the company added a baghouse to further control PM. The calciners had an uncontrolled emission rate of 1125 – 1425 ppmv SO<sub>x</sub>, corrected to 7% O<sub>2</sub>. With the use of the wet scrubber, the SO<sub>x</sub> emissions were reduced to about 160 ppmv at 90% control efficiency. With the addition of a WESP, SO<sub>x</sub> emissions were reduced by 96%, and met a standard of 35 ppmv SO<sub>2</sub>, corrected to 7% O<sub>2</sub>, on a daily average basis. The particulate fine including sulfuric acid mist was at 0.01 grains/dscf, corrected to 7% O<sub>2</sub>.<sup>40, 41</sup> The performance of BP Cherry Point coke calciners is summarized in Table 8-4.

**FIGURE 8-3**  
**FGD System for Coke Calciner at BP Cherry Point**

<sup>40</sup> Air Operating Permit - BP West Coast Products, LLC. Cherry Point Refinery Blaine, Washington, Final Modification. Northwest Clean Air Agency, September 06, 2006.

<sup>41</sup> Eliminating a Sulfuric Acid Mist Plume from a Wet Caustic Scrubber on a Petroleum Coke Calciner, Charles Brown and Paul Hohne of VECO Pacific Inc., Environmental Progress, Vol. 20, No. 3, October 2001.



**TABLE 8-4**  
**Performance of Wet Scrubber and WESP**  
**for BP Cherry Point Coke Calciners**

Equipment:	Combination of Wet Scrubber and WESP
Processing Rate:	1,301 tons per day
Control Efficiency:	<del>96%</del> 97% - 98%
Emission Rate:	0.14 lb SO <sub>x</sub> per ton coke
Outlet Concentration:	35 ppmv Limit (Test Results: 10 -12 ppmv)

### 8.4 Proposed BARCT Level and Emission Reductions

Given the facts that the dry scrubber at BP Wilmington designed up to 90% efficiency could perform at 98% - 99% control efficiencies to achieve emission rates ranging from 0.21 lb – 1.64 lb SO<sub>x</sub> per ton calcined coke; and that a combination of wet scrubber and wet ESP can achieve 96% control efficiency with an emission rate of 0.14 lb SO<sub>x</sub> per ton calcined coke, staff believe that further emission reductions from coke calciner is possible. Staff will continue to evaluate the potential BARCT level (e.g. ≤0.5 lbs/ton), emission reductions, cost effectiveness, and report the findings in Part II and Part III of the Preliminary Draft Staff Report.

## Chapter 9 - Portland Cement Manufacturing

### 9.1 Process Description

There are two Portland cement manufacturing facilities in the Basin, California Portland Cement Company (CPCC) and TXI Riverside Cement Company (TXI). CPCC manufactures gray cement, and TXI manufactures white cement and produces gray cement from clinkers delivered to the facility by railcar. CPCC ranks #10 on the list of top SO<sub>x</sub> emitters in the District in 2005 with total facility emissions of 100.5 tons per year, whereas TXI is ranked #25 with total facility emissions of 0.7 tons per year. Therefore, staff will only focus on the technology to reduce SO<sub>x</sub> emissions at CPCC in this amendment.

The production of Portland cement at CPCC is a four step process presented in Figure 9-1 which includes: 1) raw materials acquisition; 2) preparation of raw materials into raw mix; 3) pyroprocessing of raw mix to make clinkers; and 4) grinding and milling of clinkers into cement.

Raw materials for manufacturing cement include calcium, silica, alumina and iron. Calcium is the element of highest concentration, and iron is raw material for gray cement but not used for white cement. These raw materials are obtained from minerals such as limestone for calcium; sand for silica; shale and clay for alumina and silica. CPCC obtains limestone from the quarry located on site. Other raw materials are delivered to CPCC by truck or rail car.

Preparing the raw mix includes crushing, milling, blending and storage. Primary, secondary and tertiary crushers are used to crush the raw materials until they are about  $\frac{3}{4}$  inch or smaller in size. Raw materials are then conveyed to rock storage silos. Belt conveyors are typically used for this transport. Roller mills or ball mills are used to blend and pulverize raw materials into fine powder. Pneumatic conveyors are typically used to transport the fine raw mix to silos for storage until it is used to the pyroprocessing..

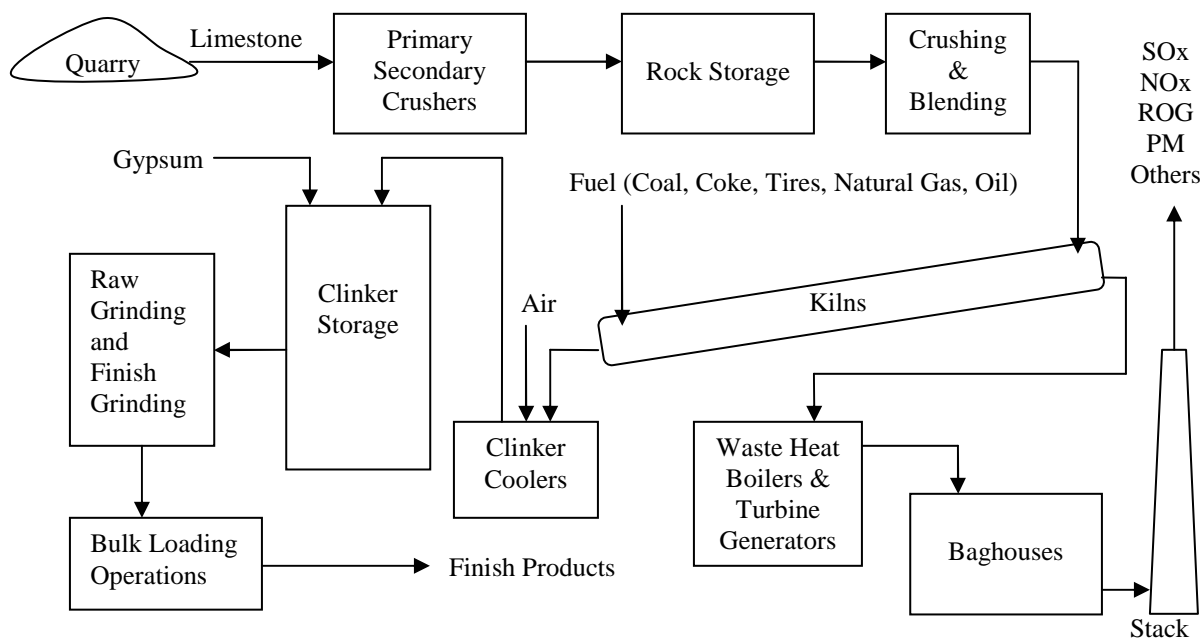
Pyroprocessing is the chemical and physical process of transforming the fine raw mix into clinkers. Pyroprocessing occurs in a rotary kiln and includes three steps:

- Evaporating free water and dehydrating to form oxides of silicon, aluminum, and iron. This process occurs in a drying and preheating zone of the rotary kiln at temperatures of about 212 °F – 800 °F;
- Calcining of calcium carbonates (CaCO<sub>3</sub>) to form calcium oxides (CaO) and carbon dioxide (CO<sub>2</sub>). This process occurs in the calcining zone of the rotary kiln at temperatures of about 1100 °F – 1800 °F; and

- Chemical reacting, melting and restructuring of materials occur between calcium oxides (CaO), silica, alumina and iron to form clinker. Clinker is a solid silicate material ranges in size from 1 inch – 2 inch diameter, and formed in the “burning” zone of the rotary kiln at temperatures of about 2200 °F – 2700 °F.

The pyroprocessing process at CPCC is called a “long dry process” consisting solely of a simple long rotary kiln. CPCC operates two rotary kilns in parallel, each is 18 ft in diameter and 500 ft in length for gray clinker. The kiln is slightly inclined and rotates on its longitudinal axis. Raw materials are fed into the upper end of the kiln while fuels are burned in the lower end. As the kiln rotates, the raw materials move slowly from the upper end to the lower end, and the combustion gases move in countercurrent direction. The residence time of raw materials in a gray cement kiln is about 2 hours – 3 hours. The hot clinker, which exits at about 2000 °F from the kiln, is quickly cooled in the clinker cooler and is conveyed to storage. Clinker is water reactive and should be protected from moisture. If clinker gets wet, it will hydrate and set into concrete. Heat used in the kiln is supplied through the combustion of different fuels such as coal, coke, oil, natural gas, and tires. The combustion gases are vented to baghouse for dust control, and dusts are returned to the process or recycled if they meet certain criteria, or is discarded to landfills.

**FIGURE 9-1**  
**Portland Cement Manufacturing Process at CPCC Colton**



Grinding and milling clinkers into cement is the last step of the manufacturing process. Up to 5% of gypsum is added to the clinker during this stage to control the setting time of cement. Other specialty chemicals are also added. After grinding and milling, the cement is pneumatically conveyed to the product silos, and either sold in bulk or is bagged.

## 9.2 Current Allocations and Emissions

### 9.2.1 Allocations

The allocations provided to CPCC in 1993, as well as the peak activities and emission factors, were presented in Table 9-1. The majority of the allocations was provided to the combustion of coal in boilers/heaters and cement kilns.

**TABLE 9-1**  
**Allocations for Kilns and Boilers at CPCC**

<b>Equipment</b>	<b>Fuel Type</b>	<b>Peak Yr</b>	<b>Emission Factor</b>	<b>Emissions (lbs/yr)</b>	<b>Emissions (tons/day)</b>
Ovens	Natural Gas	1987	0.83 lbs/mmcf	101	0.00
Boilers/Heaters	Coal	1987	3.055 lbs/ton coal	217,018	0.30
Cement Kilns	Natural Gas	1987	21.45 lbs/mmcf	1,285	0.00
Cement Kilns	Fuel Oil	1987	1.08 lbs/thousand gals	12	0.00
Cement Kilns	Coal	1987	0.351 lbs/ton coal	22,569	0.03
Cement Kilns	Natural Gas	1987	7.55 lbs/mmcf	536	0.00
Cement Kilns	Fuel Oil	1987	3.07 lbs/thousand gals	384	0.00
Cement Kilns	Coal	1987	0.013 lbs/ton coal	948	0.00
				<b>Total</b>	<b>0.33</b>

### 9.2.2 Emissions

The calendar year 2005 reported emissions from CPCC's kilns and steam boiler are presented in Table 9-2. The 2005 facility emissions are still slightly below the overall allocations. However, the emission distribution within the facility was substantially changed: the kilns generated most of the facility emissions in 2005, whereas in 1987, most of the emissions originated from boilers/heaters at CPCC. Particulate matter from the kilns and steam boiler are controlled by baghouses. Limestone used in the kilns and boiler creates an alkaline environment that promotes a direct internal absorption of SO<sub>2</sub>. Post combustion control for SO<sub>x</sub> is not currently used at CPCC.

In responding to a 2008 Survey conducted by the SCAQMD, CPCC reported that the average SO<sub>x</sub> concentrations from the two kilns were 49 ppmv at 13% O<sub>2</sub> (approximately 111 ppmv at 3% O<sub>2</sub>). The emission rate for the two kilns was approximately 0.5 lbs SO<sub>x</sub> per ton clinker..

Regarding the coal-fired steam boiler, CPCC reported that the coal-fired steam boiler has not been in operation since 2002, however CPCC may operate the boiler in the near future if circumstances in energy costs or fuel sources change. The boiler used coal and natural gas as combustion fuel. The emission rate for this coal fired boiler was approximately 7 lbs SO<sub>x</sub>/ton coal.

**TABLE 9-2**

SO<sub>x</sub> Emissions from CPCC

	Dev ID	Rating (mmbtu /hr)	SO <sub>x</sub> Level (ppmv)	2005 Emissions (tpd)	2006 Emissions (tpd)	2007 Emissions (tpd)
Kiln #2	368	260	49 (13% O <sub>2</sub> )	0.193	0.146	0.186
Kiln #1	321	260	49 (13% O <sub>2</sub> )	0.074	0.129	0.112
Steam Boiler	851	232	NA	0.002	0.000	0.000
			<b>Total</b>	<b>0.269</b>	<b>0.275</b>	<b>0.298</b>

Note: The 2005 SO<sub>x</sub> emissions were from SCAQMD database for the period from January 2005 – December 2005. The fiscal year 2006 and 2007 emissions and the SO<sub>x</sub> concentrations were reported by the facilities through the 2008 Survey.

**TABLE 9-3**  
**SO<sub>x</sub> Emission Rates**

	Emission Rate
Kilns	0.5 lbs SO <sub>x</sub> /ton clinker
Steam Boiler	7 lbs SO <sub>x</sub> /ton coal

## 9.3 Control Technology for Coal-Fired Fluidized-Bed Boilers

### 9.3.1 In-Process Control Technology

The control technologies for coal fired boilers are described abundantly in literature.<sup>42</sup> Almost all SO<sub>2</sub> emission control technologies for coal-fired boilers are post-combustion control. The exception to this universal rule is found in the fluidized bed steam boiler (Device ID 851) used at CPCC. Fluidized bed boilers generally operate at about 1500 – 1600 degree F, a lower temperature regime than other combustion systems. This temperature regime allows the addition of limestone. Limestone (CaCO<sub>3</sub>) is converted to CaO at about 1500 degree F, and CaO captures SO<sub>2</sub> to form CaSO<sub>4</sub>, which is thermodynamically stable at 1500 – 1600 degree F. A removal efficiency of about 90% SO<sub>2</sub> can be achieved with a Ca/S molar ratio of 2 to 2.5, which also varies from application to application, and depends on the sulfur content of the fuel, reactivity of the limestone, and the operation of the boiler.

### 9.3.2 Dry and Wet Scrubber

Post-combustion control for SO<sub>2</sub> is accomplished by scrubbers. A calcium- or sodium-based reagent is typically used in a scrubber to absorb SO<sub>2</sub>. Sulfate or sulfite formed are either disposed, or further processed for commercial use. Scrubbers are commonly classified based on the process conditions (wet versus dry); the product utilization (throwaway versus saleable); and the reagent utilization (once-through versus regenerable). Scrubbers are widely used in

<sup>42</sup> Assessment of Control Technology Options for BART-Eligible Sources – Steam Electric Boilers, Industrial Boilers, Cement Plants, and Paper and Pulp Facilities. Northeast States for Coordinated Air Use Management (NESCAUM) in partnership with the Mid-Atlantic Northeast Visibility Union (MANE-VU), March 2005.



commercial applications such FCCUs (Chapter 3), utility/industrial boilers/heaters (Chapter 4), sulfur recovery and tail gas treatment (Chapter 5), sulfuric acid manufacturing (Chapter 6), container glass manufacturing (Chapter 7), and coke calcining (Chapter 8). Please refer to these chapters for further descriptions on this technology.

### 9.3.3 Costs and Cost Effectiveness Reported in Literature

Both wet and dry scrubbers are widely used in the U.S. for coal-fired utility boilers. The control efficiency, costs, and cost effectiveness reported abundantly in literature are provided in Table 9-3 and 9-4.

**TABLE 9-3**  
**SO<sub>x</sub> Control Technology for Boilers ≥ 250 mmbtu/hr**

Type	Type of Control	Control Efficiency	Cost Effectiveness
Coal Fired	Dry Scrubber	90% - 95%	\$1,622 - \$3,578
	Wet Scrubber	90% - 99%	\$1,881 - \$3,822
Oil Fired	Dry Scrubber	90% - 95%	\$1,841 - \$5,219
	Wet Scrubber	90% -99%	\$1,956 - \$5,215

Note: The data in this table are from *Best Available Retrofit Technology (BARCT) for Selected Non-Electric Generating Units (EGU) Source Categories*, MACTEC Federal Programs, Inc. developed for Lake Michigan Air Directors Consortium (LADCO), June 28, 2005.

**TABLE 9- 3**  
**SO<sub>x</sub> Control Technology for Coal-Fired Boilers**

Source	Type of Control	Control Efficiency	Capital Costs	Cost Effectiveness
Utility Boilers	Dry or Wet Scrubber	90%	\$180/kW for >600 MW units \$350/kW for 200-300 MW	\$200 - \$500 per ton SO <sub>x</sub> removed
Industrial Boilers	Dry Sorbent Injection	40%	\$8,600 - \$26,000 per mmbtu/hr	Not Estimated
	Spray Dryer Absorber	90%	Double of the costs for dry sorbent injection	\$400 - \$4000 per ton SO <sub>x</sub> removed
	Wet Scrubber	90%	50% higher than spray dryer absorber	Not Estimated

Reference: Assessment of Control Technology Options for BART-Eligible Sources – Steam Electric Boilers, Industrial Boilers, Cement Plants, and Paper and Pulp Facilities. Northeast States for Coordinated Air Use Management (NESCAUM) in partnership with the Mid-Atlantic Northeast Visibility Union (MANE-VU), March 2005

## 9.4 Control Technology for Cement Kilns

SO<sub>x</sub> emissions from a cement kiln are generated from 1) combustion of sulfur in fuel, and 2) oxidation of sulfides (e.g. pyrites) in the raw materials. Fuel switching, process alterations, dry and wet scrubbers are commercially available control technologies to reduce SO<sub>x</sub> emissions

from a cement kiln.<sup>43, 44</sup> Table 9-4 presents the control efficiency for each technology and a brief description for each technology is presented below.

**TABLE 9-4**  
**Available Control Technology for Dry Cement Kilns**

Type of Control	Control Efficiency
Fuel Switching and Process Alterations	0 – 100%
Spray Dryer Absorber	55% - 90%
Wet Scrubber	90% - 99.9%

Reference: *Assessment of Control Technology Options for BART-Eligible Sources – Steam Electric Boilers, Industrial Boilers, Cement Plants, and Paper and Pulp Facilities*. Northeast States for Coordinated Air Use Management (NESCAUM) in partnership with the Mid-Atlantic Northeast Visibility Union (MANE-VU), March 2005.

### 9.4.1 Fuel Switching

Cement kilns at CPCC use coal, coke, natural gas, oil and tires as combustion fuel. When the fuel sulfur levels in the primary fuels are high, switching to a lower sulfur content fuel is an appropriate strategy. However, this strategy may not be sufficient if the fuel sulfur content is much less than the sulfur content of the kiln feed (e.g. limestone). In this case, staged combustion with mid-kiln injection of a low-sulfur fuel, or high pressure air, may need to be considered. A post-combustion add-on control device may also be needed to further reduce SO<sub>2</sub> emissions.

### 9.4.2 Process Control

The following process control can be used to reduce SO<sub>x</sub> emissions from the calciner kilns:

- It has been found that having sufficient oxygen to stabilize the alkali and calcium sulfate compounds formed in the burning zone of the rotary kiln minimizes SO<sub>x</sub> formation. The downside of this technique is that it can generate more NO<sub>x</sub>.
- It has been found that avoiding flame impingement in the burning zone, avoiding flame impingement on the clinker, or improving distribution of kiln feed to equalize temperatures in the kiln can minimize SO<sub>2</sub> formation.
- It has been found that when alkali is in excess of sulfur, SO<sub>2</sub> can be retained in clinker as alkali sulfate. In addition, reducing the amount of pyritic sulfur, or organic sulfur, in raw materials can lower the SO<sub>x</sub> emissions substantially. The downside of this technique is that

<sup>43</sup> Assessment of Control Technology Options for BART-Eligible Sources – Steam Electric Boilers, Industrial Boilers, Cement Plants, and Paper and Pulp Facilities. Northeast States for Coordinated Air Use Management (NESCAUM) in partnership with the Mid-Atlantic Northeast Visibility Union (MANE-VU), March 2005.

<sup>44</sup> *Best Available Retrofit Technology (BARCT) for Selected Non-Electric Generating Units (EGU) Source Categories*, MACTEC Federal Programs, Inc. developed for Lake Michigan Air Directors Consortium (LADCO), June 28, 2005.

the amount of alkali added, or the amount of pyretic sulfur removed, are often limited by the product specifications or market and economic factors.

### 9.4.3 Lime or Limestone Spray Dryer Absorber

Lime and limestone contains calcium, in the form of calcium carbonate ( $\text{CaCO}_3$ ), which reacts with  $\text{SO}_2$  and captures  $\text{SO}_2$  to form of calcium sulfate ( $\text{CaSO}_4$ ). Water is typically sprayed into the feed at the end of the kiln or introduced through dilution air at the air coolers. Two most common spray dryer absorbers are the RMC Pacific's Alkaline Slurry Injection System and the EnviroCare Microfine Lime System. The RMC Pacific uses a hydrated lime as scrubbing agent. The captured sulfur compounds are returned as a portion of the raw material feedstock to the roller mill, which results in no scrubber effluent or sludge disposal. The process has obtained efficiencies ranging from 55% to 65%. The EnviroCare uses water suspension of finely pulverized calcium hydroxide  $\text{Ca}(\text{OH})_2$  as scrubbing agent. Lime injection rate can be optimized through a feedback control loop from an  $\text{SO}_2$  monitor which helps to reach a  $\text{SO}_x$  removal efficiency of 90% or more.

### 9.4.4 Wet Scrubber

Wet scrubbing is a technique applicable to all types of cement kilns to remove  $\text{SO}_x$  and particulate matter simultaneously. A wet scrubber is usually installed downstream of the baghouse and uses limestone as absorbent. The most common system is the DynaWare scrubber, developed by Monsanto, installed by Fuller Company, and used on several cement kilns in the U.S. Limestone slurry containing 20% limestone and 80% water is produced in a mixing tank and sprayed countercurrent to the gas flow, cools the gases, reacts with  $\text{SO}_2$  to form calcium sulfite ( $\text{CaSO}_3$ ), calcium sulfate ( $\text{CaSO}_4$ ), and gypsum which in turn precipitate at the bottom of the absorbing tower and must be disposed of. A single-stage DynaWave scrubber in full-scale operation has a reported  $\text{SO}_2$  removal efficiency of about 90%, and a multiple-staged unit may achieve 99.9% control efficiency. Please refer to Chapter 5 for further description on DynaWave scrubber.

## Costs and Cost Effectiveness

Since wet and dry scrubbers are commonly used to further control  $\text{SO}_x$  from the cement kilns, the costs and cost effectiveness of these technologies are abundantly available in literature, and are summarized in Table 9-5 and 9-6.

**TABLE 9-5**  
**Costs for Control Technology for Dry Cement Kilns**

Source	Clinker Capacity (tpy)	Spray Dryer		Wet Scrubber	
		Capital Cost (\$/ton clinker)	Annual Operating Cost (\$/ton clinker)	Capital Cost (\$/ton clinker)	Annual Operating Cost (\$/ton clinker)
Medium Kiln	600,000	\$39.75	\$14.79	\$31.83	\$17.21

Large Kiln	1,200,000	\$23.17	\$9.43	\$20.42	\$13.05
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Note: (1) For comparison, CPCC Colton kiln #1 capacity is approximately 45 tons clinker per hour or 394,200 tons clinker per year based on a source test conducted in 2005, and an assumption that the kiln is operated 24 hours a day, 365 days a year. (2) The data in this table are from *Assessment of Control Technology Options for BART-Eligible Sources – Steam Electric Boilers, Industrial Boilers, Cement Plants, and Paper and Pulp Facilities*, Northeast States for Coordinated Air Use Management (NESCAUM) in partnership with the Mid-Atlantic Northeast Visibility Union (MANE-VU), March 2005.

**TABLE 9-6**  
**Control Efficiency and Costs for Control Technology for Dry Cement Kilns**

Source	Dry Scrubber		Wet Scrubber	
	Control Efficiency	Cost Effectiveness (\$/ton SO <sub>2</sub> removed)	Control Efficiency	Cost Effectiveness (\$/ton SO <sub>2</sub> removed)
Small Kiln	90%-95%	\$2,000 - \$6,917	90%-99.99%	\$2,030 - \$6,861
Medium Kiln	90%-95%	\$1,925 - \$7,379	90%-99.99%	\$2,004 - \$6,831
Large Kiln	90%-95%	\$1,881 - \$7,201	90%-99.99%	\$1,990 - \$6,816

Reference: *Best Available Retrofit Technology (BARCT) for Selected Non-Electric Generating Units (EGU) Source Categories*, MACTEC Federal Programs, Inc. developed for Lake Michigan Air Directors Consortium (LADCO), June 28, 2005.

## 9.5 Proposed BARTC Level and Emission Reductions

Given the facts that wet or dry scrubbers can be used to further reduce the emissions from cement kilns and coal-fired fluidized bed boilers, staff will continue to evaluate the potential BARCT levels for these two group of equipment, estimate potential emission reductions, cost effectiveness, and report the findings in Part II and Part III of the ~~Preliminary~~ Draft Staff Report.

## ~~Chapter 10 – Costs and Cost Effectiveness Analysis~~

~~(To Be Developed)~~

# ~~Chapter 11 – Proposed Rule Amendments~~

~~(To Be Developed)~~

## ~~Chapter 12 – Impact Assessment~~

~~(To Be Developed)~~

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## APPENDIX I-A – 2005 SO<sub>x</sub> RECLAIM EMISSIONS

**TABLE I-A-1**  
**2005 SO<sub>x</sub> Emissions at SO<sub>x</sub> RECLAIM Facilities**

Facility ID	Facility Name	Cycle	Emissions (tons per year)	Emissions (tons per day)	Cumulative Percentage
131003	BP WEST COAST PROD.LLC BP CARSON REFINERY	2	679.4	1.86	0.19
800363	CONOCOPHILLIPS COMPANY	2	421.2	1.15	0.3
114801	RHODIA INC.	1	410.7	1.13	0.42
800370	EQUILON ENTER., LLC, SHELL OIL PROD. U S	1	363.6	1	0.52
800030	CHEVRON PRODUCTS CO.	2	362.5	0.99	0.62
800089	EXXONMOBIL OIL CORPORATION	1	333.5	0.91	0.71
800026	ULTRAMAR INC	1	312.8	0.86	0.8
800362	CONOCOPHILLIPS COMPANY	1	210.7	0.58	0.85
131249	BP WEST COAST PRODUCTS LLC,BP WILMINGTON	1	130.1	0.36	0.89
800181	CALIFORNIA PORTLAND CEMENT CO	2	100.5	0.28	0.92
7427	OWENS-BROCKWAY GLASS CONTAINER INC	1	74.7	0.2	0.94
108701	SAINT-GOBAIN CONTAINERS, INC.	1	55.9	0.15	0.95
8547	QUEMETCO INC	1	37.3	0.1	0.96
124838	EXIDE TECHNOLOGIES	1	36.9	0.1	0.97
117247	EQUILON ENTERPRISES, LLC	1	31.2	0.09	0.98
800183	PARAMOUNT PETR CORP	1	22.6	0.06	0.99
35302	OWENS CORNING ROOFING AND ASPHALT, LLC	2	7.6	0.02	0.99
800264	EDGINGTON OIL COMPANY	2	6.7	0.02	0.99
115389	AES HUNTINGTON BEACH, LLC	2	6.4	0.02	1
40196	GUARDIAN INDUSTRIES CORP.	2	6.1	0.02	1
16642	ANHEUSER-BUSCH INC., LA BREWERY	1	5.4	0.01	1
42775	WEST NEWPORT OIL CO	1	2.3	0.01	1
119104	CALMAT CO	1	1.1	0	1
800182	RIVERSIDE CEMENT CO	1	0.7	0	1
21887	KIMBERLY-CLARK WORLDWIDE INC.-FULT. MILL	2	0.4	0	1
45746	PABCO BLDG PRODUCTS LLC,PABCO PAPER, DBA	2	0.1	0	1
800372	EQUILON ENTER. LLC, SHELL OIL PROD. US	2	0.1	0	1

**Total                      3621                      9.92**

(Note: There are 27 facilities out of total 33 facilities listed in this table. Staff is in the process of gathering the emissions for the remaining 6 facilities and will update this table in the future.)

**TABLE I-A-2**  
**2005 SOx Emissions of Top Seven Groups of Equipment**

Group	Fac Name	Description	Fuel Type	2005 Emissions (lbs)	2005 Emissions (tpd)
1	B	REGENERATOR, FCCU		755399.17	1.03
1	F	REGENERATOR, FCCU		447175.34	0.61
1	A	REGENERATOR		281211.84	0.39
1	D	REGENERATOR		195964.32	0.27
1	D	BOILER		30445.34	0.04
1	C	REGENERATOR		703085.36	0.96
1	E	REGENERATOR, FCCU		0	0.00
1	E	BOILER, CO WASTE HEAT, FCCU		181757.45	0.25
<b>Total for 6 FCCUs</b>					<b>3.55</b>
2	B	HEATER, CRUDE OIL DISTILLATION	REF_GAS	57649.9	0.08
2	D	BOILER	REF_GAS	25516.55	0.03
2	D	HEATER	REF_GAS	47760.79	0.07
2	D	FURNACE	REF_GAS	32123.51	0.04
2	C	HEATER	REF_GAS	76489.74	0.10
2	C	HEATER	REF_GAS	64590.83	0.09
2	C	BOILER	REF_GAS	45844.81	0.06
2	C	BOILER	REF_GAS	43162.12	0.06
2	C	HEATER	REF_GAS	30440.13	0.04
2	C	HEATER	REF_GAS	28672.09	0.04
2	C	HEATER	REF_GAS	27970.11	0.04
2	E	HEATER, COKING PROCESS	PROCESS GAS, REF GAS	48332.59	0.07
2	E	HEATER, CRUDE UNIT	PROCESS GAS, REF GAS	39770.77	0.05
2	E	HEATER, COKING PROCESS	PROCESS GAS, REF GAS	39577.84	0.05
2	E	BOILER, HYDROGEN GENERATION	REF GAS, NAT GAS	28868.34	0.04
2	E	BOILER, STEAM GENERATION	REF GAS, PROCESS GAS FROM SCRUBBER	26484.59	0.04
<b>Total for 16 boilers/heaters (1 currently not in operation)</b>					<b>0.91</b>
3	EE	INCINERATOR (C54), CONTROL EQUIP FOR ABSORBER OF SULFUR RECOVERY UNIT	REF_GAS, NAT GAS, PROCESS GAS	32995.62	0.05
3	EE	INCINERATOR (C56), CONTROL EQUIP FOR ABSORBER OF SULFUR RECOVERY UNIT	REF GAS, NAT GAS, PROCESS GAS	11974.31	0.02
3	B	CONTROL DEVICE (C-910) THERMAL OXIDIZER	REFINERY GAS, NATURAL GAS, WASTE GAS	114337.58	0.16
3	B	CONTROL DEVICE, THERMAL OXIDIZER	REFINERY GAS, NATURAL GAS, WASTE GAS	111676.16	0.15
3	F	OXIDIZER		116994.68	0.16
3	A	THERMAL OXIDIZER (D927), TAIL GAS IN SULFUR PRODUCTION UNIT	NATGAS, REF GAS	75220.2	0.10
3	A	THERMAL OXIDIZER (D927), TAIL GAS IN SULFUR PRODUCTION UNIT	NATGAS, REF GAS	62774.65	0.09

TABLE I-A-2 (Continued)

Group	Fac Name	Description	Fuel Type	2005 Emissions (lbs)	2005 Emissions (tpd)
	A	THERMAL OXIDIZER (D911), TAIL GAS IN SULFUR PRODUCTION UNIT	NATGAS, REF GAS	47309.99	0.06
	D	OXIDIZER		112186.65	0.15
	C	INCINERATOR (C456), SULFUR RECOVERY UNIT NO 2, TAIL GAS INCINERATOR	REF GAS, NAT GAS	7518.47	0.01
	C	INCINERATOR (C436), SULFUR RECOVERY UNIT NO 1, TAIL GAS INCINERATOR	REF GAS, NAT GAS	7005.95	0.01
<b>Total for 11 SRU/Tail Gas Units</b>					<b>0.96</b>
	B	FURNACE, SULFURIC ACID PLANT	FUELOIL, NAT_GAS, SULFUR	821456.88	1.13
	A	REACTOR, SULFURIC ACID PRODUCTION, COMBUSTION CHAMBER	PROCESS GAS	28304	0.04
	A	REACTOR, SULFURIC ACID PRODUCTION, COMBUSTION CHAMBER	REFGAS, NATGAS	443.05	0.00
<b>Total for 3 Sulfuric Acid Manufacturing Reactors/Furnace</b>					<b>1.16</b>
	BG	FURNACE	NAT_GAS	55242.68	0.08
	BG	FURNACE, MELTING	NAT_GAS, OXY-FUEL, PROPANE, GLASS	61637.19	0.08
	BG	FURNACE, MELTING	NAT_GAS, OXY-FUEL, PROPANE, GLASS	26411.28	0.04
	SG	FURNACE, MELTING	FUEL OIL, NAT_GAS, OXY FUEL, GLASS	93706.37	0.13
<b>Total for 4 Container Glass Melting Furnaces</b>					<b>0.32</b>
	BW	KILN, ROTARY, CALCINER PET COKE	NATURAL GAS, DIESEL FUE:	257392.34	0.35
<b>Total for 1 coke calciner</b>					<b>0.35</b>
	CC	KILN	COAL, COKE, FUEL OIL, NAT GAS, TIRE	140815.54	0.19
	CC	KILN	COAL, COKE, FUEL OIL, NAT GAS, TIRE	54045.06	0.07
	CC	BOILER, STEAM GENERATION, CIRCULATING FLUIIZED BED	COAL, COKE, NAT GAS	1561.82	0.00
<b>Total for 2 cement kilns</b>					<b>0.27</b>
<b>TOTAL 7 CATEGORIES OF EQUIPMENT</b>					<b>7.53</b>

**END OF DOCUMENT**