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Fluid Catalytic Cracking Case Study: BP
Whiting Refinery**

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Selective Catalytic Reduction of NO_x from Fluid Catalytic Cracking - Case Study: BP Whiting Refinery

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ABSTRACT

One of the newest examples of selective catalytic reduction (SCR) in service on a fluid catalytic cracking unit (FCCU) is scheduled to begin operation in October 2003 at the BP Products North America Inc. (BP) refinery in Whiting, Indiana. This application is a step beyond the typical refinery boiler/heater/furnace case since treatment of nitrogen oxides (NO_x) in the regenerator flue gas must account for the other atmospheric contaminants generated simultaneously in the FCCU process. Such conditions typically include a high particulate loading. One must also be constantly aware of the possibility of process upsets. This paper presents a case study that relies upon the experience gained and lessons learned from numerous prior FCCU installations dating back to 1986. That experience has contributed in no small degree to the design and anticipated start-up of the present unit. Following a brief review of the FCCU process itself, the source of NO_x in the process is discussed along with the origin and treatment in general of the other atmospheric contaminants. An extensive list of previous installations of this type by the SCR system supplier and the SCR catalyst manufacturer is provided, along with operational details from those cases. Successful performance as documented herein allows the owner/operator to meet regulatory requirements in a safe, reliable, and cost-effective manner. The design, start-up, and operation of the subject installation will add to that experience base.

INTRODUCTION

The fluid catalytic cracking unit (FCCU), also known as the *cat cracker*, is the central process at the heart of a typical high-conversion refinery producing gasoline. It cracks large gas oil molecules into smaller molecules within the gasoline range plus light gases, other liquid products, and petroleum coke.

Unfortunately, without abatement, a refinery's cat cracker also generates atmospheric contaminants as undesired by-products. In the paragraphs that follow, we shall see how this disparate nature can be reconciled to satisfy both the motorist's demand for gasoline and the public mandate for clean air in a proven, cost-effective manner as we share our experience concerning selective catalytic reduction (SCR) for control of nitrogen oxides.

REGULATORY BACKGROUND

In General

The FCCU is the biggest single source of atmospheric pollution in an oil refinery, primarily from sulfur oxides and particulates.¹ Although on a lesser scale, half of the NO_x (oxides of nitrogen = nitric oxide, NO, + nitrogen dioxide, NO₂) in a refinery is estimated to originate from the FCCU.

A recent refining survey² lists slightly over 130 petroleum refineries operating in the Continental U.S., Alaska, and Hawaii. Approximately 100 of these employ some form of fluid catalytic cracking in the refining process. Total cat cracking feed at a given refinery ranges from 2,300 to 227,000 barrels per calendar day (b/cd) (0.37 to 36.1 million liters/cd). Median and average values are 54,000 and 56,000 b/cd, respectively, or 8.6 and 8.9 million liters/cd in metric units.

A number of refiners in the U.S. are operating under consent agreements with EPA to reduce air emissions from their cat crackers, including NO_x emissions. As indicated in these decrees, EPA believes that a NO_x emission concentration of 20 ppmvd (annual average at 0 % oxygen, O₂) is achievable by an SCR system.³

In Particular

In January 2001, BP and the United States Environmental Protection Agency (U.S. EPA) reached an agreement⁴ in which BP agreed to reduce emissions above and beyond currently controlled levels at each of the BP refineries located in the U.S. Under the agreement, BP will implement innovative pollution control technologies greatly reducing emissions of NO_x and sulfur dioxide (SO₂) formed during the process of refining crude oil into petroleum products.⁵ BP is recognized as a leader in progress toward reducing these and other atmospheric contaminants through corporate initiatives involving the production of clean fuels and greenhouse gas reductions.⁶

The consent decree involves five[†] U.S. refineries including Whiting. For the Whiting Refinery, this equates to an improvement in emissions reductions of SO₂ of over 82 % and over 51 % in

[†] At the time of the agreement, BP owned and operated eight refineries within the U.S. Since that date three refineries (located in Yorktown, VA; Mandan, ND; and Salt Lake City, UT) have been sold.^{2,7}

NOx. These emissions reductions will be accomplished through a series of capital investments on various units throughout the refinery over the next few years at an estimated cost of over 80 million dollars.⁶ Agreed-upon cat-cracker emission controls are summarized in Table 1.⁴

Table 1. Summary of Air Contaminant Emission Controls

Unit Designation ^A	Control Method		
	NOx ^B	CO	SO ₂ ^B
FCCU 500	Addition of NOx adsorbing catalyst in conjunction with low-NOx combustion promoter (if and when CO promoter is used)	Control to a limit of 500 ppmvd	Wet gas scrubber (WGS) to be installed by 2006 In the interim, SO ₂ to be controlled by addition of SO ₂ adsorbing catalyst
FCCU 600	SCR with a design level of 20 ppmvd @ 0 % O ₂ or lower to be completed and operating following the turnaround in calendar year 2003	Control to a limit of 500 ppmvd	SO ₂ to be controlled by addition of SO ₂ adsorbing catalyst beginning no later than June 30, 2003

Notes:

- A. There are two FCCUs in service at the BP Whiting refinery, with a combined charge capacity of 156,800 b/cd as of January 1, 2003.²
- B. A continuous emissions monitoring system (CEMS) must be used to monitor NOx and SO₂ from each unit.

PROJECT PARTICIPANTS

The case study of this presentation describes elements of the project to install SCR on FCCU 600. Participants include BP, the owner/operator; Mitsubishi Power Systems, the SCR system supplier; and Cormetech, the SCR catalyst manufacturer. A brief background for each follows.

BP

BP p.l.c. is the holding company of one of the world's largest petroleum and petrochemicals groups.⁸ Main activities are exploration and production of crude oil and natural gas; refining, marketing, supply, and transportation; and manufacturing and marketing of petrochemicals. BP's roots stretch back to the late 19th century and the start of systematic oil exploration in the United States and the Middle East. BP has well-established operations in Europe, North and South America, Australasia, and Africa.

Following a series of mergers and acquisitions with Amoco, ARCO, Burmah Castrol, and Vastar, by 2001 BP had become the largest oil and gas producer and the second largest gasoline retailer in the U.S. BP's products are marketed under the Amoco and ARCO brands in the U.S. and the BP brand in the U.S. and the rest of the world. BP is also one of the world's largest marketers of aviation fuel and a major supplier of fuels and lubricants to the global shipping industry. BP has strong marketing positions in petrochemicals in North America, Europe, and the Far East and operates large-scale chemicals manufacturing plants in the U.S. and elsewhere.

The Whiting Refinery (Figure 1),⁹ built in 1889, is currently one of five[#] BP refineries in the U.S. It occupies 1,400 acres (5.7 sq km) stretching through three communities in Northwest Indiana, southeast of Chicago, Illinois. It operates 24 hours per day, 365 days per year, and employs about 1,200 people. It can process more than 400,000 barrels (63.6 million liters) of crude oil per day into 16 million gallons (60.6 million liters) of product, over half of it gasoline. The refinery transports feeds and products via barge, rail, truck, and pipelines. The BP Whiting Refinery will be the **owner and operator** of the subject SCR unit.

Mitsubishi

Mitsubishi Power Systems, Inc. (MPS) is the **SCR system supplier** for this project. Its corporate origins can also be traced back to the late 19th century.¹⁰ Beginning in 1976, Mitsubishi in Japan has installed nearly 300 SCR systems on a wide variety of industrial and utility applications. In North America, MPS has added over 160 SCR installations since 1986. These include gas turbines, utility boilers, refinery boilers and furnaces, and the refinery FCCUs discussed in this presentation.¹¹

[#] As stated in a previous footnote, three of the others involved in the Consent Decree (at Yorktown, VA; Mandan, ND; and at Salt Lake City, UT) have been sold.^{2,7}

Cormetech

Cormetech, the **SCR catalyst manufacturer**, is a joint equity venture of Corning Incorporated and Mitsubishi Heavy Industries, Ltd. Founded in 1989, the company is the leading U.S.-based source of SCR catalysts. With manufacturing facilities in Durham, North Carolina and Cleveland, Tennessee, Cormetech services the power-generation, refining/petrochemical, and industrial processing industries worldwide with products to safeguard the environment.¹²⁻¹⁴

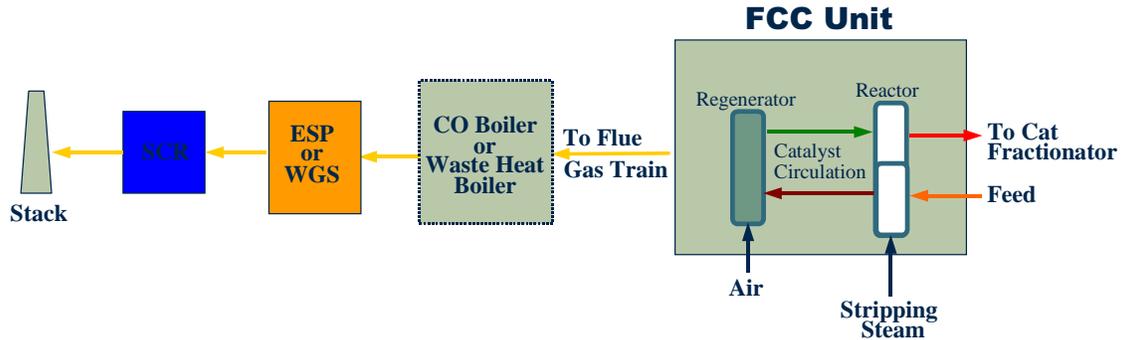
Figure 1. Whiting Refinery – Aerial Photograph



FCC PROCESS DESCRIPTION

The fluid catalytic cracking (FCC) process¹⁵⁻²² is conducted in a pair of fluidized-bed vessels containing catalytic cracking catalyst, which circulates continuously from one vessel to the other through a set of transfer lines (Figure 2). Those vessels are referred to as the *reactor* and *regenerator*, respectively. Conditions are summarized in Tables 2 and 3. Somewhat different configurations of the basic hardware are currently in use,^{19,23,24} having evolved separately from the joint cooperative effort at the time of World War II to develop the process.^{19-21,23,25-33} Reactor and regenerator may sit side by side or one atop the other.

Figure 2. Generic Process Flow Diagram for FCCU and Ancillary Flue-Gas Treatment



FCC Cracking Catalyst

Fresh cat cracking catalyst is a porous silica-alumina material, white in color and finer than most beach sand. It was originally produced from naturally occurring minerals but is now made from synthetic crystalline zeolites and amorphous materials. Individual FCC particles exhibit a microspheroidal shape. Its particle-size distribution approximates log-normal, with a range from close to 0 to over 100 micrometers (μm , or microns) and a mass median diameter (50 % point) of approximately 50 to 80 μm .³⁴⁻³⁵

When a gas or vapor is passed upward through a bed of FCC catalyst at a velocity in excess of the pressure drop needed to support the bed, it becomes “fluidized” and exhibits the properties of a liquid. Fluidization occurs when the pressure drop across the bed is sufficient to support the weight of the particles in the stream of flowing fluid. For FCC catalyst, the minimum, or incipient fluidization velocity is on the order of 0.001 to 0.01 ft/sec (0.0003-0.003 meters/sec).^{36,37} It is two to three orders of magnitude below normal operating velocities.^{33,38-40} Further information on fluidization is available elsewhere.⁴¹⁻⁴⁶

Table 2. Summary of Typical FCCU Conditions^A

Condition	Reactor	Regenerator
Temperature, °F (°C)	<u>Bed or Riser:</u> 900-1050 (480-565) <u>Oil Feed:</u> 500-800 (260-425)	<u>Partial-Burn Unit (w CO Boiler):</u> 1100-1250 (595-675) ^B <u>Full-Burn Unit:</u> 1250-1500 (675-815) ^B
Pressure, psig	10-35 (Range of Cited References)	8-40 (Range of Cited References)
Catalyst Condition: Entering Leaving	Regenerated Spent	Spent Regenerated
Fluidizing Gas	Hydrocarbon Vapors Steam (for feed atomization and steam stripping)	Air Flue Gas Some Steam
Atmospheric Pollutants at Exit of Regenerator or CO Boiler:		
CO	--	<u>Partial Burn:</u> In % Range <u>Full Burn or Leaving CO Boiler:</u> <500 ppm
Particulates	--	See Table 3.
SO _x	--	Low to hundreds of ppm or more, depending on feed, hydro- desulfurization, and additives
NO _x	--	<100-500+ ppm

Notes:

- A. Entries in the table were compiled from the references cited in the text.
- B. Temperature leaving CO Boiler or Waste Heat Boiler can be as low as 600 °F (315 °C).

Table 3. Summary of FCCU Particulate Matter (PM) at Various Locations

Location	Collection Efficiency (%)	Particulate Loading at Exit (mg/Nm ³)	Particle Size at Exit (µm)	Remarks ^A
Regenerator Bed	--	See table below.	Avg. 50-80 in dense bed	At some point above 90 µm average particle size (APS), fluidization becomes poor.
Regenerator Cyclones (1 st - and 2 nd - Stages Combined)	99.995 (combined)	≥ 200	Avg. 20 or less	See Appendix A.
3 rd -Stage Cyclones	70-90 (conventional) 40-50 (multiclones)	50, 75, or 100-150	Avg. 5 (98 % < 10 µm)	Usually located in pressure vessel outside regenerator. Works best for particle sizes >10 µm. Do not depend on to meet a permit limit of <50 mg/Nm ³ .
4 th -Stage Cyclones	--	--	--	Used for solids separation when transporting the <u>underflow</u> from collection hopper in vessel containing 3 rd -Stage Cyclones.
Electrostatic Precipitator (ESP)	90-98	10-50	2-5	Probably the most commonly employed technology downstream of the regenerator cyclones. Effective on particles down to 1 µm.
Wet Gas Scrubber (WGS)	90-95	≤ 50	--	Also removes SO _x .
Baghouse	Virtually 100 %	< 25	--	Baghouses have not been used except on small slip-streams for testing or as a substitute for 4 th -Stage Cyclones noted above. (See Appendix A.)

Entrainment from Regenerator Bed			
Regenerator Superficial Velocity (ft/sec)*	2	3	4
Particulate Loading at Cyclone Inlet (lb/ft ³)*	0.2	1.0	2.0
* 1 ft/sec = 0.3048 meters(m)/sec; 1 lb/ft ³ ≅ 1.6 x 10 ⁷ mg/Nm ³ , or 16 kg/Nm ³			

Note:

A. Data are presumed not to include upset conditions.

Source: Information compiled largely from NPRA Q&A Transcripts (1990-1999).⁴⁷

The Reactor

In the FCC process, a hydrocarbon feed, usually in the gas oil range, is vaporized upon contact with hot catalyst in the transfer line to the reactor. Cracking of large molecules takes place on the surface and in the pores of the catalyst in the transfer line or in the reactor itself. The desired products from cat cracking pass upward in the vaporized state through the reactor bed and out of the reactor to be separated into gas and various liquids (gasoline components and middle distillates) in the cat fractionator distillation column downstream. The chemistry of hydrocarbon cracking reactions is discussed at length in the reference materials.⁴⁸⁻⁴⁹

One (undesired) product of cracking is coke, a condensed hydrocarbon somewhat deficient in hydrogen. Coke has a black color and contains carbon, hydrogen, sulfur, nitrogen, and metals. Sulfur, nitrogen, and metals originating in crude oil tend to accumulate in the heavier liquid fractions and coke produced during refining. Metals include nickel, which enhances coke formation, and vanadium, which catalyzes oxidation of sulfur dioxide (SO₂) to sulfur trioxide (SO₃) during combustion of sulfur compounds. The sulfur and nitrogen in the coke are in the form of large, heavy organic molecules. Buildup of coke and its accompanying metals on the catalyst interferes with the desired cracking reactions and must be continuously removed to some low level. This takes place in the regenerator.

Catalyst from the reactor riser or reactor vessel is constantly moving downward, into, and through the transfer line to the regenerator. Simultaneously, catalyst continues to circulate from the regenerator to the top of the reactor. Before entering the transfer line, catalyst leaving the reactor first encounters a stripping section, where steam is injected to strip the hydrocarbon vapors remaining in, on, and around the catalyst particles. Catalyst leaving the reactor on its way to the regenerator is said to be *spent*, and is termed *regenerated* when leaving the regenerator (Table 2).

The Regenerator

In the regenerator, the coke is burned off to prepare the catalyst for its return to the reactor. Compressed air is fed to the bottom of the regenerator for this purpose. Coke on regenerated catalyst (CRC) attains a very low percentage but is not removed all the way to zero, and *regenerated* catalyst is a light gray to black color.

The heat generated by the combustion reaction vaporizes the feed oil and supplies the energy necessary for the endothermic cracking reactions taking place in the reactor vessel plus whatever heat losses occur. If possible, the unit operates naturally in heat balance through control of the temperatures and circulation rate. Otherwise, heat can be added by preheating the feed, and it can be removed by making steam via heat exchange with the hot flue gas leaving the regenerator or by means of a catalyst cooler.⁵⁰

Atmospheric Contaminants from the Regenerator

Atmospheric contaminants are formed in the regenerator, either chemically during the combustion process or physically from the carryover of catalyst particles entrained in the regenerator flue gas. These include carbon monoxide (CO), catalyst particles (particulate matter, PM, or total suspended particulates, TSP), sulfur oxides (SO_x = sulfur dioxide, SO₂, + sulfur

trioxide, SO₃), and oxides of nitrogen. Origin and treatment of CO, PM, and SO_x are considered in Appendix A; NO_x is discussed below. A recent reference provides further details.³

NO_x IN FCCU REGENERATOR FLUE GAS

Source of NO_x

NO_x levels in the flue gas from a commercial FCCU regenerator are typically on the order of 100 or less to 500+ ppm⁵¹⁻⁵⁵ and predominantly in the form of nitric oxide (NO).⁵⁶ Organic nitrogen compounds constitute between about 0.05 % up to 0.5 % of FCCU feed. Although the majority of this nitrogen appears in the FCCU products, nearly half of the nitrogen ends up in the coke on catalyst. When the coke is burned, the nitrogen is liberated in various forms.

During regeneration, 70-90 % of the nitrogen in the coke is reduced to N₂, and the other 10-30 % makes nitric oxide. This is so-called *fuel NO_x*,⁵⁷ coming from the condensed organic nitrogen compounds in the coke. These include aromatic-ring structures containing nitrogen atoms, amines, pyridine compounds, pyrrole derivatives, and amides. Temperatures in the regenerator are too low to produce any appreciable *thermal NO_x*, from the combination of the N₂ and O₂ in the combustion air; a maximum of 10-30 ppm of thermal NO_x is estimated even if chemical equilibrium were to be achieved.⁵¹⁻⁵²

The organic nitrogen compounds in the coke break down into such species as ammonia (NH₃), hydrogen cyanide (HCN), nitrous oxide (N₂O), nitric oxide (NO), and molecular nitrogen (N₂). Ammonia from commercial FCCUs has been measured by others in a few cases at levels of 400 to 1000 ppm.⁵⁸ The presence of HCN in the flue gas from a commercial regenerator has also been reported.⁵⁹ Molecular nitrogen is thought to arise from reaction of NO with carbon (C) or carbon monoxide (CO), thereby decreasing the amount of NO.

Increasing the amount of oxygen in the regenerator decreases both the carbon on regenerated (CRC) (i.e., the coke) and the carbon monoxide. It also causes the remaining coke to become richer in nitrogen species, which tend to burn last after the carbon. Both effects lead to an increase in regenerator-exit NO with increasing O₂.⁶⁰ For a full-burn unit, NO_x is formed at excess O₂ in one overall step. Full-burn units operate in an oxidizing environment at higher excess O₂ to produce lower concentrations of NH₃ and HCN and to oxidize these intermediates to NO.

Under the reducing conditions of a partial-burn unit with an excess CO concentration, the organic nitrogen compounds in the coke react to elemental nitrogen (N₂), reduced nitrogen compounds such as ammonia and HCN, and some NO_x. When combustion is completed in a CO Boiler, the reduced nitrogen compounds form more NO_x,⁶¹ and thermal NO_x plus perhaps some fuel NO_x are added from the CO Boiler fuel.⁶² Low-NO_x burners are available for CO Boilers and will lower the thermal NO_x output but not the fuel NO_x.⁶³

In summary, a NO_x concentration up to hundreds of ppm can be expected in either case, depending on the overall excess O₂ concentration in the regenerator and the nitrogen level in the cat-cracker feedstock. NO_x from the regenerator may also be affected by higher local O₂ concentrations there caused by poor mixing.

NOx-Abatement Technology

Prospective techniques for NOx removal fall into several categories: hydrodesulfurization, FCCU catalyst additives, scrubbing, and chemical reaction such as selective non-catalytic reduction (SNCR) and selective catalytic reduction (SCR). Hydrotreating of FCCU feed will decrease feed nitrogen, nitrogen in the coke on catalyst, and consequently NOx from the regenerator, but it is costly and unlikely to be done for NOx abatement alone.

The amount of NO is enhanced by the presence of a platinum-based CO combustion-promoter and depressed by an additive specifically engineered to decrease NOx.⁵⁵ Such NOx-control additives can also be used for fine-tuning of other NOx-abatement techniques. However, since regenerator NOx is primarily NO with its a low solubility in aqueous scrubbing solutions, NOx removal in a conventional WGS for abatement of sulfur oxides and particulates is limited.⁵⁶

SNCR reacts ammonia or urea with NOx to produce molecular nitrogen and water vapor. No catalyst is employed, and reaction takes place in a narrow high-temperature window, compared with SCR.⁶⁴ This technology has been demonstrated on various boilers, heaters, furnaces, and incinerators as well as on a coal-fired fluidized-bed boiler.⁶⁵ An application on a refinery FCCU in California is mentioned briefly in a later section.⁶⁶ NOx-removal efficiencies are typically much lower than with SCR. The advantages of SNCR are that there is no catalyst to plug or foul and the price is cheaper. The disadvantage is a much lower NOx-removal efficiency.

THE SCR PROCESS

In this process (Figure 3), the oxides of nitrogen NO and NO₂, commonly known as NOx, are reacted with ammonia (NH₃) in the presence of a flow-through honeycomb catalyst to give nitrogen (N₂) and water vapor (H₂O). Reaction stoichiometry with ammonia, injected upstream, depends on the relative amount of each oxide and whether or not oxygen (O₂) is present. For applications such as FCCU flue gas containing excess oxygen and parts-per-million (ppm) concentrations of NO in excess of NO₂,⁵⁶ the equations given in the figure apply. In the absence of competing side reactions, the theoretical molar ratio of NH₃ reacted to NOx destroyed is 1.0.

The ammonia employed in the SCR process is either anhydrous (100 % concentration, a cryogenic liquid under high pressure) or aqueous, in which the ammonia is diluted with water. Typical aqueous ammonia concentrations range from 19-29 %. The choice of which type of ammonia to use is determined by the owner/operator and is specified during the design phase. Both types are common in SCR systems.

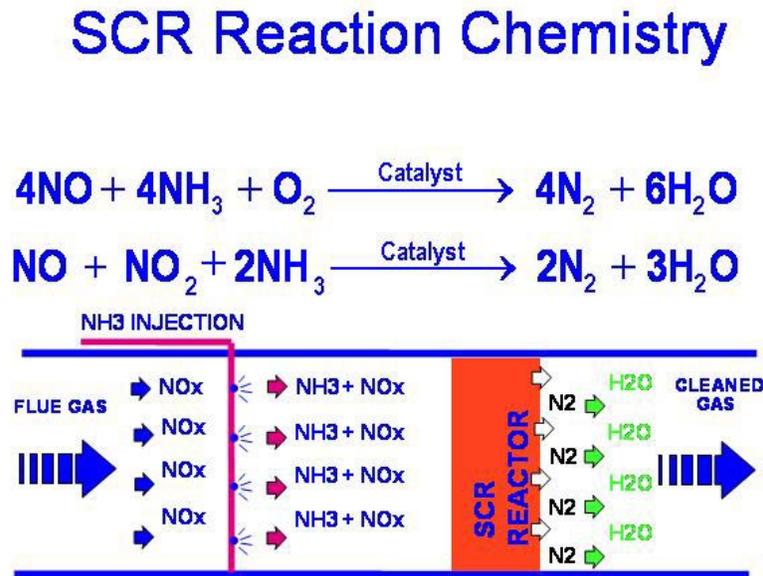
The use of anhydrous ammonia allows all the SCR process piping, fans, and flow control valves to be smaller and, therefore, less expensive. However, many communities have very restrictive regulations concerning the transportation of anhydrous ammonia through population centers, its storage, and use. Consequently, obtaining the necessary permits for anhydrous ammonia may be prohibitive. Permitting for aqueous ammonia is typically much easier.

Ammonia beyond that required to participate in the SCR reactions appears in the SCR effluent and is designated as *ammonia slip*. Sufficient catalyst must be present to provide the required degree of NOx removal at an acceptable level of ammonia slip.⁶⁷⁻⁶⁸ NOx-removal efficiency depends ultimately on the amount of catalyst; the NH₃-to-NOx ratio; and the local distribution of ammonia, NOx, and flow across the SCR inlet.

To ensure proper distribution of ammonia and NOx at the inlet to the SCR catalyst, physical cold flow modeling or computational fluid dynamic analysis is performed prior to finalizing the design of the SCR reactor housing. In physical cold flow modeling, a clear-plastic scale model of the proposed ducting, housing and ammonia injection is built. By matching the dynamic pressure and/or Reynolds number, the flow model will accurately simulate the bulk flow characteristics present in the actual ducting/housing. In this manner, the model will demonstrate the flow distribution at the SCR catalyst.

If the flow in the model is shown to be maldistributed in such a way that would make it difficult to achieve the desired NOx reduction, turning vanes or perforated plates can be added. These can then be adjusted until the desired flow distribution is achieved, and the modifications would be incorporated into the full-scale design. Computational fluid dynamic analysis performs the same function by means of mathematical modeling.

Figure 3. NH₃ Reacts with NO_x



The Presence of Other Pollutants and/or Control Devices for Their Removal

SCR treatment of nitrogen oxides in FCC regenerator flue gas must also account for the other atmospheric contaminants generated simultaneously in the FCCU process. In addition, design of the SCR must address the pollution control devices installed to abate those contaminants. A series of pollution control devices, such as SCR for NO_x control, an electrostatic precipitator (ESP) for particulate removal, etc., for example, can be placed in various locations and arranged in many different configurations to treat FCC regenerator flue-gas. No two treatment-configurations will be the same, especially on a retrofit unit.

The presence of other flue-gas contaminants and/or pollution control devices may affect NO_x removal. Effects may be good or bad. For example, ammonia can be used both to remove NO_x

in SCR or SNCR and to enhance removal of FCCU catalyst fines in an ESP. Such an interaction in ammonia usage was reported for an unidentified California refinery.⁶⁹

SCR NOx removal upstream with sulfur oxides present runs the risk of SCR catalyst fouling by ammonium sulfate ((NH4)2SO4) and/or bisulfate (NH4HSO4), depending on conditions. An upstream location also risks plugging and the scouring action of entrained particulate matter. However, installation of SCR for NOx removal downstream of a wet gas scrubber (WGS) for removal of sulfur oxides would require energy-intensive reheat.* There is also the possibility of poisoning by pH-control agents (containing sodium or calcium) carried over in any liquid-droplet entrainment that might occur.

Performance of SCR has been demonstrated on FCCUs as described below.

SCR EXPERIENCE ON FCCU FLUE GAS

Selective catalytic reduction (SCR) NOx removal on the FCC process has been practiced in Japan since the 1980s⁷⁰ and most recently at the ExxonMobil (formerly Mobil) refinery in Torrance, California.⁶⁷ Seven Mitsubishi-supplied installations in Japan and three more in the U.S. are listed in Tables 4 and 5, updated from a previous presentation.⁷¹ Flue-gas flows range from about 75,000 to over 530,000 Nm³/hr [47,000-330,000 SCFM (standard ft³/min @ 60 °F, 1 atm)]. Cormetech provided the SCR catalyst for a number of these installations, including Torrance. Each new design, including BP Carson and BP Whiting, benefits from this accumulated experience.

Table 4. SCR Supply Record for FCC

	Plant Name	Start of Operation
1	Saibu Oil Co. Yamaguchi	Apr. 1986
2	Showa Yokkaichi Oil Co. Yokkaichi	June 1988
3	Nippon Petroleum Refining Co. Negishi	June 1992
4	Idemitsu Petrochemical Co. Hokkaido	Oct. 1994
5	Kyokutou Petrochemical Co. Chiba	Nov. 1994
6	Showa Yokkaichi Oil Co. Yokkaichi-R	July 1995
7	Koa Osaka	June 1997
8	Mobil (now ExxonMobil) Torrance, California	Apr. 2000
9	BP Carson (California)	Mar. 2003 (scheduled)
10	BP Whiting (Indiana)	Oct. 2003 (scheduled)

* For typical conditions of regenerator flue gas at 600 °F (315 °C), and 10 % moisture, calculations with simplifying assumptions show the adiabatic saturation temperature to be approximately 150 °F (65 °C) as the gas is cooled by the evaporating water, the water is heated by the hot flue gas, and the scrubber water evaporates upto its saturation concentration in the flue gas. This temperature is well below the operating temperature of the SCR process.

Table 5. Flue Gas Conditions for FCCUs

Plant Name	Flue Gas Flowrate (Nm ³ /hr)	Temp (°C)	Inlet NO _x (ppm)	Outlet NO _x (ppm)	O ₂ (%)	Removal Efficiency (%)	NH ₃ slip (ppm)	SO _x (ppm)	SO ₃ (ppm)	Particulate (mg/Nm ³)
FCCU #1	75,600	369	300	60	1.9	80	5	200	20	60
FCCU #2	83,000	380	500	250	1.0	50	10	120	10	200
FCCU #3	530,367	288	350	28	2.0	92	20	25	3	120
FCCU #4	147,500	360	160	16	2.0	90	5	586	46	520
FCCU #5	171,600	360	250	50	2.0	80	5	1050	65	400
FCCU #6	75,317	343	168	100	3.4	41	5	83	7	114
FCCU #7	331,000	399	874	78	1.8	91	10	930	93	150
FCCU #8	151,600	340	120	10	3.0	92	3	150	9	700
FCCU #9	379,063	288	155	10	0.7	94	20	232	12	36
FCCU#10	350,777	371	100	18	1.8	82	20	126	14	294

Updated from Gentile, K., "BACT/LAER Technology for Tier II," Slides from Panel Discussion at the 2000 NPRA Annual Environmental Conference, San Antonio, TX (Sept. 10-12, 2000).⁷¹

Potential problems previously noted⁷¹ for SCR on FCC plants are listed below:

- Higher SO₃-to-SO₂ ratio leading to formation of ammonium salts
- Possible corrosion of downstream equipment from SO₃ formation in the SCR
- High particulate loading
- Increased catalyst pitch (along with soot-blowers or sonic horns) required to minimize plugging
- Carryover of oil mist under upset conditions in the FCCU

The effects of the sulfur species and high particulates are to be expected from phase equilibria or physical considerations. In the absence of SO₃ in the flue gas, the operating temperature range for SCR is 400-750 °F (204-399 °C). However, as the SO₃ concentration rises, so does the minimum operating temperature. As an example, on an FCC unit with 500 ppm of SO₃ in the flue gas, the minimum operating temperature may be as high as 650 °F (343 °C). Operating below this temperature would allow the injected ammonia to react with the SO₃, resulting in the formation of ammonium sulfate ((NH₄)₂SO₄) and/or bisulfate (NH₄HSO₄). Either of these salts can foul or plug downstream equipment, including the SCR catalyst itself. The effects of the fouling or plugging can be reversed, in large part, by simply returning the unit to an operating temperature above the prescribed minimum.

The presence of SO₃ in the flue gas can also lead to the formation of sulfuric acid, H₂SO₄. If the flue gas temperature falls below the sulfuric acid dew point (150-175 °C, 303-347 °F),⁷² SO₃ and water (H₂O) will condense out to form the acid, and corrosion of downstream equipment may result.

As with oil-fired or coal-fired boiler SCRs, the loading and characteristics of the particulate that will reach the SCR are the main determining factors in the selection of catalyst pitch for an FCC

application. If the particulate loading is substantial enough, it may also be advisable to install either soot-blowers or sonic horns above each layer of SCR catalyst. Fortunately, the particulate coming out of a FCC regenerator is not as “sticky” as the particulate from an oil-fired or coal-fired combustion source. As such, the FCC particulate has less of a tendency to adhere to the surface of the SCR catalyst, thereby minimizing the blockage of reaction sites and/or an increase in pressure drop.

In the event that the FCC regenerator should experience a “reversal” or some other episode resulting in extraordinary FCC catalyst carryover, oil mist may be deposited onto the SCR catalyst surface. The oil may be oxidized in place, raising the catalyst surface temperature to prohibitively high levels. During such an occurrence, the catalyst will most likely be sintered. Under extreme cases, the SCR catalyst will be destroyed beyond its ability to meet NO_x-reduction compliance levels. The metal substrate of a coated SCR catalyst can ignite with ambient air following such an upset, as occurred at a utility boiler installation using a competitor’s catalyst. Therefore, homogeneous ceramic catalyst is preferred for reasons of safety.⁷¹

Torrance, California Background Information

Installation No. 8 in Gentile’s presentation⁷¹ (Table 4) is at the Mobil (now ExxonMobil) Refinery in Torrance, California. It is both the largest and the most recent unit on the list to have begun operation.⁷¹ The Torrance Refinery is located approximately 19 miles (37 km) (*sic*) southwest of Los Angeles, in the Los Angeles Air Basin, as noted in a paper presented by Mobil in 1994.⁶⁶ Information on the Torrance operation was obtained from that presentation and other sources in the public domain.

The Torrance Refinery contains a cat cracker built under license from UOP.^{19,23,24,73} FCC charge capacity at Torrance is stated as 90,500 b/cd (14.4 million liters/cd) as of January 1, 2003.² Hydrotreated FCC feed is preheated in an external furnace before entering the reactor; the regenerator is followed by a third-stage separator, expander turbine, CO Boiler, and ESP, with a waste heat boiler at the tail end.⁶⁶ Results of a commercial-scale test of a Mobil-developed CO combustion promoter (defined and explained in Appendix A) at Torrance were reported in 1979,⁷³ and a promoter may still be in use there.

Selective non-catalytic reduction (SNCR), a Nalco Fuel Tech NO_xOut system utilizing urea, was installed on the FCCU CO Boiler (760-1010 °C, 1400-1850 °F) in the 1988 time frame.⁶⁶ The temperature window quoted in the paper for the urea-based SNCR is 760-1149 °C (1400-2100 °F), and 760-972 °C (1400-1780 °F) for the competing Exxon Thermal De-NO_x SNCR process utilizing ammonia.

As others have found,⁵¹⁻⁵⁵ inlet NO_x was said to originate from the organically bound nitrogen in the FCCU gas oil feed combined with the thermal NO_x produced by combustion of CO and auxiliary fuel in the CO Boiler. For this particular plant, the Nalco technology provided a day-to-day NO_x-removal efficiency between 40-55 %, with performance-test results under controlled conditions as high as 66 %. The original NO_x-reduction goal was 24 %.

However, SCR is capable of reducing NO_x from the FCCU by over 90 %. (See Table 5 above.) Replacement of the SNCR unit by SCR enables the refinery to comply by 2003 with refinery-wide NO_x emission limitations mandated by the South Coast Air Quality Management District

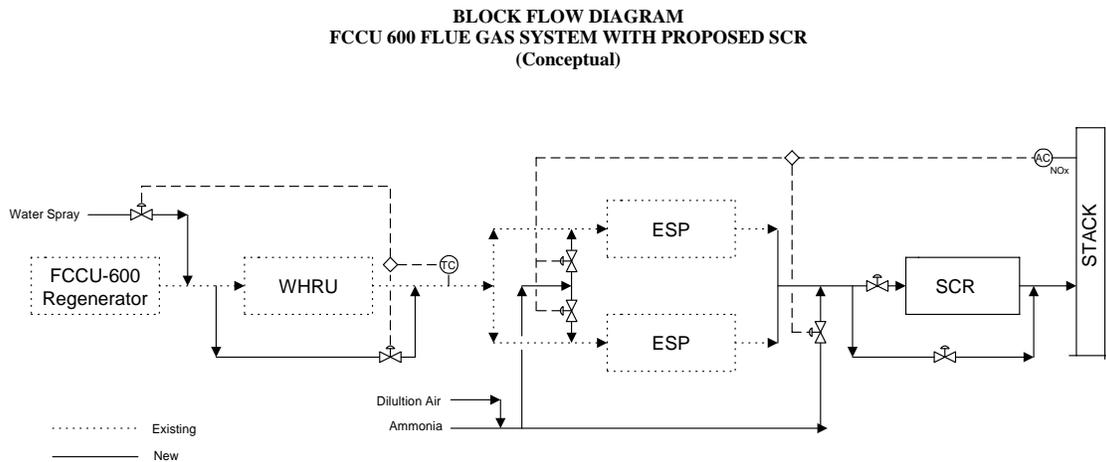
(SCAQMD), the air quality jurisdiction that includes Torrance. Permissible ammonia slip from SCR's at the time of the Mobil presentation was 20 ppm⁶⁶ but is much less today.

FCCU 600 REGENERATOR FLUE-GAS TREATMENT AT BP WHITING

Figure 4, taken from the SCR permit application, illustrates the process flow for the new SCR on the FCCU 600 at the BP Whiting Business Unit in Whiting Indiana. In the FCCU process, coke (mostly carbon, hydrogen, sulfur and nitrogen) must be burned off the FCCU catalyst in the Regenerator to restore the catalyst activity. Fuel NO_x is formed in the process as a by-product of the combustion reaction.

Flue gases from the Regenerator are first cooled in the Waste Heat Recovery Unit (WHRU), which generates process steam. The WHRU is a sensible heat boiler without supplemental firing. The flue gases are then treated in the Electrostatic Precipitators (ESPs) to control particulates before entering the new SCR to reduce NO_x. Flue gases from the new SCR exhaust to the atmosphere through a stack. When the WHRU is out of service, quench water will be used to cool the flue gases to the desired operating temperature of the ESPs.

Figure 4. Flue-Gas Treatment for BP Whiting FCCU 600



The nitrogen oxides (NO_x) and oxygen (O₂) contained in the FCCU flue gas will react with injected ammonia on the SCR catalyst to produce environmentally benign nitrogen and water vapor, as discussed earlier. The SCR is designed to reduce the flue gas NO_x concentration to 20 ppmvd at 0 % O₂, or lower, as required by the Consent Decree reached between BP and the EPA.

To ensure that the SCR operates above its minimum temperature for NO_x control and that the flue gas is below the design temperature of the ESPs, a temperature-controlling bypass valve is installed around the WHRU. When it is necessary to bypass the WHRU completely, water sprays (not shown) are used to ensure that the ESP inlet temperature is below its design temperature.

Some of the ammonia is injected before the WHRU to enhance both the particulate removal and opacity control in the ESPs. Also, if the NOx is rather high (above 40 ppmv) it appears that a portion of the inlet NOx is catalytically reduced by the metals that are present naturally on FCCU catalyst dust. Because of space limitations and mixing concerns, it was necessary to inject the ammonia before the WHRU rather than immediately upstream of the ESPs. Several unit tests were performed to confirm that stack opacity decreases and NOx does not increase when ammonia is injected ahead of the WHRU as shown in Figure 4. (Sometimes, NOx decreases.)

Finally, a bypass is installed around the new SCR to allow its catalyst to be replaced without shutting down the FCCU.

SUMMARY

- The FCCU is the biggest single source of air pollution in an oil refinery.
- A number of refiners in the U.S. are operating under consent agreements with EPA to reduce emissions, including NOx from the FCCU.
- NOx from the FCCU regenerator originates from the organically bound nitrogen in the FCCU feed (fuel NOx). This is augmented by thermal NOx from a CO Boiler, if present, plus additional fuel NOx from any nitrogen compounds in the CO Boiler supplemental fuel.
- SCR is capable of reducing these NOx emissions by over 90 %.
- SCR design must account for other, accompanying atmospheric contaminants, such as particulates and sulfur oxides, and/or the control devices installed for their removal.
- SCR design must also address upset conditions.
- Experience gained and lessons learned from numerous SCR FCCU installations of various sizes tabulated here date back to 1986.
- The largest and most recent of these to have begun operation is located at a refinery in Torrance, California.
- The two others listed in this presentation are scheduled for start-up shortly.

ABOUT THE AUTHORS

Gerald D. Bouziden has been with BP (Amoco) since 1975. He is a Senior Process Design Engineer at the Whiting Business Unit. In his current job he focuses on modifications for BP oil refineries. His recent work has involved coker expansions, major crude unit modifications, FCCU upgrades, wastewater treatment upgrades, tutoring of both new and experienced engineers, and various environmental engineering projects. Currently, he has been involved on the project team to install a SCR on the FCCU 600 Unit at Whiting IN, and has critically reviewed SCR designs for other BP FCCUs.

Mr. Bouziden has had considerable experience in the application of SCR NO_x control technology for FCCUs through a variety of stack tests and unit tests. He has examined the necessary requirements for SCRs to ensure that the adequate upstream equipment is in place. The tests were conducted to develop a sound design basis for successful application of a new SCR at FCCU 600.

Mr. Bouziden received both his BS degree in Chemical Engineering and his Masters of Engineering degree from Iowa State University.

J. Kurtis Gentile has been with the Mitsubishi group of companies since 1995. In his role as a Senior Project Engineer he focuses primarily on proposal preparation and sales/marketing efforts in the area of petroleum refining. Most recently his work has centered on the application of SCR technology as applied to Fluidized Catalytic Cracking Units (FCCUs).

Mr. Gentile has considerable experience in the field of air pollution control, specifically in the field of NO_x reduction. Prior to his working with Mitsubishi, Mr. Gentile was a start-up engineer with Noell, Inc. He also worked with Joy Environmental as a project engineer in the advanced technology department and with Refractory Composites where he worked in the development of Low-NO_x burners.

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Robert G. Kunz joined Cormetech, Inc. in April 2001 as Technical Project Manager. He supports sales and marketing efforts in the petroleum refining and petrochemical industries by advising on business development strategy, development of training materials, technical report writing, and evaluation of laboratory and field data.

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APPENDIX A

ATMOSPHERIC POLLUTANTS – ORIGIN AND TREATMENT

Carbon Monoxide (CO)

Carbon monoxide is formed in the regenerator from incomplete combustion of the carbon content of the coke on catalyst. There are, in general, two types of regenerators: the so-called *partial-burn units* built up to about 1972, and the *full-burn units* constructed thereafter. In a partial-burn unit, coke is burned to CO₂ plus CO in the percent range with little or no excess O₂. These older units produce a regenerator flue gas with a CO/CO₂ ratio of around 1.0 and containing up to 10 % CO. Since combustion of CO to CO₂ liberates about 2.5 times as much heat as combustion of carbon to CO, this allowed a lower regenerator temperature and easier control but resulted in an excess of CO emitted to the atmosphere (Table 2).

To meet an EPA-mandated effluent limit of 500 ppm, the flue gas is processed in an external combustion device, known as a *CO Boiler*, in which auxiliary fuel is fired to incinerate the excess CO in the regenerator effluent to within acceptable limits. Auxiliary fuel is necessary because of the very low heating value (20-40 Btu/SCF) of the regenerator flue gas.⁷⁴ Heat is recovered from the CO Boiler flue gas by making steam.

Full-burn units operate with a higher excess O₂ in the regenerator itself and produce CO within the ppm range. These run hotter, burn more coke off the catalyst, but are more difficult to control. Where a CO Boiler is not necessary to control CO emissions, the regenerator flue gas is cooled in an unfired heat exchanger, termed a *waste heat boiler*. Full-burn units may be built to employ a two-stage combustion in separate zones.⁷⁵

Certain additives can also be blended in with the cracking catalyst to facilitate CO combustion in the regenerator. These employ a platinum-based CO oxidation catalyst, or *promoter*, to enhance CO combustion in the regenerator dense phase and are also used to prevent excessive temperatures from so-called *afterburning* of CO remaining in the dilute phase.

Particulate Matter (PM)

In both the reactor and regenerator vessels, the fluidizing gas (hydrocarbon vapors in the reactor and air/flue gas in the regenerator) carry the smaller catalyst particles, the so-called *finer*, out of the bed and upward into the dilute phase above the bed. The process of expelling particles from the bed is known as *elutriation*, the phenomenon of solids being carried by the gas *entrainment*, and the height between the expanded bed and the exit of the vessel the *freeboard*. The particle- and gas-mixture in the freeboard is termed the *dilute*, or *lean phase*, to distinguish it from the *dense phase* within the bubbling bed below. Elutriation and entrainment increase with increasing gas *superficial* velocity, the volumetric flow rate divided by the cross-sectional area of the empty vessel. Superficial velocity in the regenerator is nominally in the range of 1-6+ ft/sec.³⁸⁻⁴⁰ Entrainment data for regenerator superficial velocities between 2 and 4 ft/sec at the inlet to the cyclones is shown at the bottom of Table 3.³⁸

The larger entrained particles typically settle out on their own. The smaller particles, or *finer*, are captured mechanically and returned to the bed in cyclone separators to prevent excessive loss of bed material. Finer are contained in the original FCC catalyst particle-size distribution and are created during operation by particle breakdown, fracture of larger particles, and/or abrasion and erosion of their outer surface, processes known as *attrition*.

Cyclones in the Regenerator

The smaller of the finer expelled from the regenerator bed enter two stages of inertial separators in series to effect their capture. These separators are known as *cyclones*. Gas containing suspended particulates enters the first stage (primary), passes on to the second stage (secondary), and vents out the top of the second stage. Multiple sets of such cyclones are arranged in parallel to handle the total gas flow.

Some of the particles entering the cyclones are captured and are returned by gravity to the bed. The others escape from the regenerator, and unless further abated downstream, are emitted to the atmosphere via the regenerator flue-gas stack. Collection efficiency is higher in the first stage than in the second stage since the larger particles are collected preferentially. Typical combined collection efficiency from both stages is 99.995 %. Typical operating conditions, solids loadings, and particle sizes are shown in the main body of Table 3.

The reactor vessel is also provided with two stages of cyclones. The catalyst particles escaping from the reactor cyclones are caught in the cat fractionator and form a slurry in the bottom of that column. These do not constitute an emission to the atmosphere.

Third-Stage Cyclones⁷⁶⁻⁷⁷

In some cases, the exhaust gas from the regenerator is let down in pressure through a turbo-expander for power recovery. The resulting high-pressure steam can also be used to drive a steam turbine. To protect the blades in the turbo-expander from the sand-blasting effect of the entrained catalyst, a third stage of cyclones (tertiary) is added. These cyclones are usually contained in a separate pressure vessel external to the regenerator.

The extremely fine particles captured here may or may not be returned to the circulating catalyst inventory. Emissions from transporting the collected catalyst finer in the underflow of the external collection vessel are treated with a fourth stage of cyclones or another particulate-collection device, such as an electrostatic precipitator (ESP) or a baghouse.

Third-stage cyclones cannot be used by themselves for environmental control except in those jurisdictions where the regulations are sufficiently lenient. The usual devices for particulate control to meet regulatory requirements are electrostatic precipitators or wet scrubbers.

Electrostatic Precipitator (ESP)

These are a commonly employed particulate clean-up technology downstream of the regenerator cyclones. They are high efficiency collection devices and are effective on particles down to 1 μm (Table 3). They cause minimal pressure drop and can operate over a wide range of temperatures but appear to be limited to a maximum of 650 °F (345 °C) when placed upstream of a CO Boiler.⁷⁸

In an ESP, flue gas flows between large vertical parallel plates carrying an electrical charge. Finely divided solids in the gas acquire the opposite charge and migrate toward the plates, where they are collected in solid sheets. Periodically, the plates are gently rapped to dislodge the solids into a collection hopper below. As with 3rd-Stage Cyclones, some or all of the precipitator catch may or may not be recycled to the regenerator.

Collection efficiency for FCC catalyst fines is enhanced by ammonia and/or SO₃ either already occurring in the flue gas or injected upstream.

Wet Gas Scrubber (WGS)

This device contacts the flue gas with an atomized spray of fine droplets, which encapsulate suspended solids and absorb sulfur oxides and any other water-soluble contaminants.⁷⁹⁻⁸¹ The droplets themselves, much larger than catalyst fines, are then separated from the gas by cyclonic action in a second vessel. Particulate collection of 90-95 % is regularly achieved (Table 3) along with SO_x removals of 90-99 %. An alkali, such as caustic, soda ash, or lime, is added to the recirculating scrubbing liquor to control pH.

Baghouses

A baghouse contains multiple filter bags or socks through which a gas must flow. The bag material must be able to withstand the temperature of the gas. Solids in the gas impinge upon the mesh surface of the bag and form a filter cake. This cake then acts as the collecting surface.

As solids build up on the surface, pressure drop increases. Periodically, triggered either by time on line or by pressure drop, the bags are cleaned by shaking or by a reverse pulse of air. Groups of bags are arranged in separate chambers to allow the service flow to continue while some of the bags are taken off line for cleaning. It is also important to be able to isolate and replace bags which have sprung a leak, without having to shut down the entire system.

Baghouses can collect solids at virtually 100 % efficiency. However, they are not known to have been used on FCCUs except on small slip-streams for testing or as a substitute for 4th-Stage Cyclones on the 3rd-Stage Cyclone catch (Table 3); a baghouse on an FCCU would adversely affect the delicate regenerator pressure balance and is said to increase the risk of upset and possibly catastrophic loss of control.⁸²

Sulfur Oxides (SO_x)¹

Sulfur in the cat-cracker feed makes its way to several locations: 70-95 % leaves the reactor overhead in the liquid products or as H₂S in the product gas, and the remaining 5-30 % ends up in organic thiophenes and similar structures in the coke. When the coke is burned off in the regenerator, up to hundreds or even thousands of ppm of SO_x can result. Sulfur trioxide (SO₃) can constitute up to about 10 % of the total SO₂ (sulfur dioxide) plus SO₃,⁸³ compared to a typical natural-gas combustion effluent with an SO₃ content of only 1-3 %. Metals in the coke, especially vanadium, will cause a greater SO₃ to SO₂ ratio than normal.

There are four options to lower SO_x to acceptable levels: use of low-sulfur feeds to the cat cracker, hydrotreating of higher-sulfur feedstocks, blending of sulfur-removal additives into the FCC catalyst, and wet gas scrubbing (WGS) of the regenerator flue gas.⁸⁴ Having to employ naturally low-sulfur materials as cat-cracker feed is restrictive, and hydrotreating to bring the sulfur level down to the same range is costly.

Catalyst additives function by enhancing the fraction of SO₃ formed upon combustion in the regenerator and then tying it up with the catalyst until the catalyst reaches the reactor. The sulfur content is then liberated as H₂S in the reactor, to be separated from the overhead product gas, rather than becoming an atmospheric pollutant emitted from the regenerator. The viability of this method in any specific case depends on the amount of sulfur removal possible at reasonable addition rates.

A WGS can remove the sulfur oxides in regenerator flue gas at the high efficiencies discussed above. Disadvantages include having to contend with a solids-laden waste scrubbing liquor requiring treatment and disposal and a water-saturated, corrosive exhaust gas at relatively low temperature (a visible steam plume) possibly containing traces of sulfuric acid.⁷²