Technology, Allowances and Credits: Components of a Sound NO_x Reduction Strategy

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This article examines several options to meet upcoming NO_x reductions of the flue gas coming from the Fluid Catalytic Cracking Unit (FCCU). Several technologies such as SCR, SNCR, and additives will be reviewed to highlight their benefits and limitations. Since every FCCU is unique in terms of feed quality and process conditions, each refiner must determine their own NO_x management solution without sacrificing the facility's operating flexibility.

An overview of allowances, credits and the current Houston/Galveston Cap and Trade program will also be provided. Trading emission reduction credits offers refiners flexibility in terms of time to get the plant into compliance as well as financial incentive for people whose facilities are in compliance and have spare credits to sell. Some refiners may elect to hedge their risk by reducing NO_x emissions and taking a long position on their emission reduction credits. The current market for these credits lacks liquidity, i.e. many buyers and many sellers. If a refiner thinks he can wait a year or two to purchase credits, the credits may not be available and if there are credits, the cost may be extremely high.

The Environmental Protection Agency is considering a plan that would require refineries, utilities and other plants to reduce nitrogen oxide emissions by 80 percent to as much as a 90 percent by 2008. In either case, refineries with a FCCU will have to change the way they currently operate the unit since it is the source of over 50% of the total NO_x emitted from the refinery.

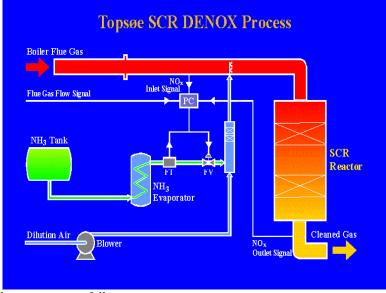
The task is intimidating since the FCCU Flue Gas flow rates are large and many of its products are used as feedstocks in downstream operations. The unit's performance has a direct economic and operational impact on the entire refinery due to the scale and scope of its products, i.e. fuel oil, distillate, high octane gasoline, olefinic LPG, refinery fuel gas and steam. The challenge for refiners when conceiving their NO_x removal strategy will be to preserve the FCCU's operational versatility and diverse yield slate.

The FCCU Flue Gas NO_x concentration typically ranges from 50 ppmvd to 400 ppmvd with an average of approximately 200 ppmvd. The proposed target of 20 ppmvd NO_x by the year 2008 associated with the Consent Decrees represents a fundamental change to the way the unit is currently operated.

Technology - SCR

Selective Catalytic Reduction (SCR) is the reaction of NO_x with ammonia NH_3 that occurs on a catalytic surface to produce N_2 and H_2O . The typical temperature range of an SCR is 400 °F to 950 °F with guaranteed NO_x removal rates of 95+%. The catalytic metals are oxide forms of vanadium and tungsten. Commercial applications of SCR range from very clean service in natural gas – fired turbines to ultra high particulate loadings (>20,000 mg/Nm³) in coal – fired utility boilers.

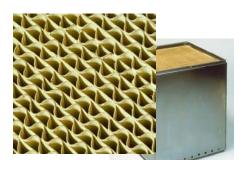
The general process flow diagram is illustrated below:



The reactions that occur are as follows:

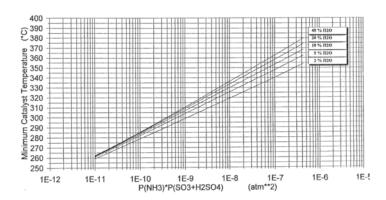
The SCR does not interfere with the cracking process as it is downstream of the Reactor and Regenerator.

Currently, there are several FCCUs equipped with SCRs throughout the world with the first one placed on – line in 1986. Normal particulate concentrations of FCCU Flue Gas are less than 500 mg/Nm³. The SCR is ideally situated in the low dust position downstream of an Electrostatic Precipitator (ESP) but can easily be designed for high dust service.



Refiner and Location	Start of SCR Operation
Saibu Oil Co. Japan	1986
Showa Yokkaichi Oil Co. Japan	1988
Nippon Petroleum Refining Co. Japan	1992
Skandinaviska Raffinaderi AB Sweden	1994
Idemitsu Petrochemical Co. Japan	1994
Kyokutou Petrochemical Co. Japan	1994
KOA Japan	1997
ExxonMobil USA	2000

Design considerations include targeted NO_x removal level, service life, pressure drop limitation, ammonia slip, space limitation, flue gas temperature, composition and SO_2 oxidation limit. SCR suppliers typically guarantee the performance of the unit for NO_x removal, service life, pressure drop, ammonia slip and SO_2 oxidation. Ammonia slip, referring to the reactant, which passes through the process, is typically guaranteed between 2 and 10 ppmv.



The reaction of SO₂ to SO₃ is undesirable because the SO₃ can react with NH₃ to form the salt ammonium bisulfate (ABS) which will foul downstream equipment and trigger high opacity readings. ABS formation is a function of temperature, ammonia partial pressure and SO₃ partial pressure. If the reactant species are abundant in a cool environment (< 500 °F), ABS formation will occur.

 SO_2 Oxidation: $2 SO_2 + O_2 \rightarrow 2 SO_3$

Ammonium Bisulfate Formation: $NH_3 + SO_3 + H_2O \rightarrow NH_4HSO_4$

Ammonium Sulfate Formation: $2 \text{ NH}_3 + \text{SO}_3 + \text{H}_2\text{O} \rightarrow (\text{NH}_4)_2\text{SO}_4$

The preceding graph describes ABS formation as a function of temperature for a specific case and is provided only for discussion as every application is unique. Corrective actions to take if the unit starts to form ABS are to increase the operating temperature of the SCR above the ABS dewpoint and verify the concentrations of ammonia slip and SO₃. ABS is a temporary foulant since elevating the operating temperature will cause sublimation to gaseous phase.

Technology - SNCR

Selective Non – Catalytic Reduction (SNCR) is the process of reacting NO_x with NH_3 at high temperatures without the aid of a catalyst to produce N_2 and H_2O . The typical operating temperature range of 1500 °F to 1800 °F is a requirement for NO_x reduction levels of 50 percent along with sufficient residence time. Excess NH_3 is required to compensate for the amount of NH_3 oxidized at these high temperatures before it has a chance to react with the NO_x . NH_3 slip in SNCR applications range from 10 to 100 ppmv.

The saving in catalyst cost is offset by the lower NO_x removal levels at higher NH₃ slip. Higher conversion levels are possible through flue gas recycling and multiple stages of NH₃ injection but these options



increase the overall cost and complexity of the system. The basic design of an ammonia injection grid is simply a series of perforated pipes connected to a manifold. The cost of this equipment is higher in SNCR than one suited for SCR due to the metallurgy required for high temperatures. Alloys containing chrome, molybdenum and nickel such a Hastelloy and Inconel are typical examples.

SNCR is not currently used in FCCU service due to low NO_x removal at temperatures below 1400 °F. In full – burn units, the flue gas must be heated within

1600 to 1800 °F to achieve NO_x removal rate of 50% and greater. For a FCCU in complete combustion, this would require a duct burner which would create more NO_x. Ammonium Bisulphate formation is much greater in SNCR due to the higher NH₃ slip.

Technology - Additives

This approach involves direct involvement of the FCCU Reactor and Regenerator. Depending on application specifics, NO_x catalyst additives are designed to achieve 30 to 70% more NO_x removal than conventional CO combustion promoters. These additives can withstand the harsh environment of the Regenerator where temperatures approach 1,400 °F in the dilute phase but do not have the same life as catalyst. Additives are typically introduced through a shot pot or an automatic loader. Catalyst vendors are also able to blend additives into the fresh catalyst they deliver to the refiner thus eliminating the need for manual dosing and automatic loaders. Suppliers recommend limiting the use of these additives to no more than 5 to 10 percent of the fresh catalyst addition rate for maintenance after an initial base load.

A benefit associated with the use of additives is flexibility. Additives can easily be added and removed from the operation depending on the refiner's needs. Some of the concerns refiners have with additives are their catalytic life which is known to be shorter than FCC catalyst, addition rates as a function of NO_x concentration and desired reduction, yield impact at higher concentrations, effectiveness in partial combustion operation and the ability to handle NO_x fluctuations. Use of a NO_x additive will increase a refiner's FCCU variable operating cost as the additive is more expensive than FCC catalyst with an average cost approaching \$20 per pound.

Refiners will not be able to meet the proposed 80% NO_x reduction using these additives. The additional cost associated with the recommended usage rate of these additives may triple the current catalyst cost resulting in negative process unit economics. Higher removal rates will require more additive that may impact yields, product quality and unit throughput.

Selecting the optimum technology or combination of technologies is very dependent on unit specifics, i.e. inlet NO_x concentration, target outlet concentration, process conditions, constraints, etc. Emissions allowances and various emissions reduction credits represent other variables to utilize when considering the refinery's overall NO_x reduction strategy.

Emissions Allowances

In an effort to achieve environmental goals, states have implemented various Cap & Trade programs. Each refiner will be given a certain amount of NO_x emission allowances each year based on their average level of annual emissions from 1997, 1998 and 1999. Future allowances decrease in line with the region's NO_x reductions.

This is not representative of all programs. It is in reference to Houston/Galveston only.

An example of an Allowance Stream in units of Tons of NO_x is provided to show the large decrease in NO_x emissions from 2002 to 2008.

Year:	<u>2002</u>	<u>2003</u>	<u>2004</u>	<u>2005</u>	<u>2006</u>	<u>2007</u>	<u>2008</u>
Allowance	1621 9	1621 9	1163 6	683 3	443 4	138.2	51.0

In the Houston/Galveston area, a facility that has the potential to produce 10 tons or more of NO_x per year is subject to the Cap & Trade program and must have allowances to offset their NO_x emissions. If the facility produces more NO_x than is allowed they must purchase another facility's surplus allowances to offset their overproduction, or their next year's allowance allocation is reduced by the exceeded amount plus 10%. Failure to comply will result in fines and possible shutdown of the offending facility. Additional allowances are obtained by creating NO_x reductions via operational changes, pollution control equipment and shutdown of non – essential facilities. The surplus can then be sold to other sites in the region or rolled forward to the next year to be used as offsets. Allowances have a life of 2 years, but must be used on a last in first out basis.

Emission Reduction Credits (ERCs)

In the Houston/ Galveston SIP (State Implementation Plan) Call Program, emission reduction credits are tradable commodities that allow the holder to emit VOC or NO_x from a stationary or mobile source within an ozone non – attainment area up to a stated level measured in tons per year. Emission Reduction Credits are very sensitive to supply and demand factors. Not only do Emission Reduction Credits expire, but due to future increasing demand, prices are set to skyrocket.

There are several types of ERCs that differ based upon the date they were issued, and as such, will have different expiration terms. A NO_x ERC issued prior to January 1^{nd} , 2001 is valid for 10 years and is transferable into allowances on a 1:1 basis. NO_x ERCs issued after January 2^{nd} , 2001 are not transferable into allowances and are valid for only up to 5 years from the date they are issued. NO_x ERCs issued after January 1^{st} , 2001 are only usable for New Source Review for environmental retirement. Post January 1^{st} , 2001 NO_x ERCs cannot be used as offsets against pollution of a facility.

Discrete Emission Reduction Credits (DERCs) are a voluntary reduction in VOC, NO_x, SO₂, PM or CO emissions from a stationary area which is created during a generation period, quantified after that period and expressed in tons. DERCs do not expire but those created before January 1st, 2005 depreciate over time. DERCs created after January 1st, 2005 do not depreciate.

DERCs are valuable because they can be used to offset new emission sources or a major modification that will increase emissions as well as cover an exceedance to a permit limit.

Mobile Emission Credits (MERCs) and Mobile Discrete Emission Reduction Credits (MDERCs) are the last two types of credits. They are created by any mobile source emission reduction and are usable as an allowance on a per ton basis in any year. MERCs and MDERCs do not expire. Mobil credits can be created through reductions on mobile sources and transferred on a one-to-one basis to stationary sources to offset pollution. For example, a retrofit that reduces NOx emissions 20% on a vehicle that emits 5 tons of NOx pollution per year will be able to bank one MDERC per year, which can be transferred or sold to a refinery for use as an allowance in any year on a one-to-one basis and they do not expire.

	Allowances Tons	ERCs Ton/year	DERCs Ton/year	MERCs Ton/Year	MDERCs Ton/Year
Issued	?	?			
Voluntarily Created			?	?	?
Expiration	?	?			
Depreciation			?		
Transfer into Allowances		?	?	?	?
Current Price		\$35,000	\$1,700		

A Houston/Galveston ERC valued at \$35,000 is relatively inexpensive compared to a San Diego ERC currently priced at \$140,000.

Environmental credits are valuable assets and must be managed accordingly. The management of these credits must take into account multiple variables which include overall position (short or long), objective (monetary or environmental), available capital, project implementation, etc.

The players in this market are not limited to refineries, chemical plants and utilities. Municipalities, cooperatives, independent power producers, banks, insurance companies and speculators seek a share of the limited credits. A Houston/Galveston ERC valued at \$35,000 is relatively inexpensive compared to a San Diego ERC currently priced at \$140,000. Investors are hoping the future value of ERCs in Houston/Galveston will approach similar prices in the next few years placing huge demand on a limited supply. Operators are hoping credits will be available.

Case Study

An economic evaluation for an SCR installed on a 70 MBPSD FCC unit was recently performed for a client. The inlet NO_x concentration of the Flue Gas was 300 ppmv dry – basis at 3% reference O2 translating to 500 tons/ Year of NO_x . Single – pass conversion scenarios of 80% and 90% were prepared for a Cost: Benefit Analysis.

80% NO_x Reduction

Total installed cost for the SCR system is \$7.0 MM that includes the SCR catalyst, reactor housing, ammonia system, process analyzer and controls. The system guarantees 80% NO_x reduction, 5 ppm NH3 slip, 1 vol.% SO₂ Oxidation, 3 inches WC pressure drop and a 4 year continuous service life. If the system is commissioned by April 1, 2004 when a required 44% NO_x reduction is required, the owner would have an excess 180 ERCs. These ERCs are tradable and at the current price of \$35,000/ERC, this results in \$6.3 MM which would offset 90% of the cost of the SCR in the first year.

On April 1,2005, 89% of the total reduction is required. Thus, the owner is short 0.5 tons/ year and would have to buy the ERC or alter the facility's operation for 2005 and 2006. The final reductions go into effect on April 1, 2007 when 100% of the target NO_x reductions are required. At that time, the owner is 50 tons/ year short and must make arrangements to offset the difference via acquisition of ERCs or facility modifications.

90% NO_x Reductions

Total installed cost for this SCR system is \$9.0 MM and includes all the previously mentioned components. Guarantees are related to 90% NO_x reduction along with the associated process parameters. If the system is commissioned by April 1, 2004, the owner would have 230 ERCs at his discretion. These ERCs are worth \$8.05 MM based on current prices and represent over 89% of the installed cost of the SCR.

On April 1, 2005, when 89% of the total reduction is required, the owner still has 49.5 discretionary ERCs. They are approximately worth \$1,7 MM in 2005 and \$1.7 MM in 2006 based upon current prices. When the final reductions go into effect on April 1, 2007, the owner is in balance with a 90% reduction target and does not need to trade ERCs to continue operations.

Conclusion

 NO_x emissions reductions of 80% or greater require suitable commercially – proven technology to achieve this goal. Since the FCC Unit emits more than 50% of the total NO_x in a modern refinery, SCR technology offers the most value considering the achievable levels of NO_x reduction, generating valuable emission reduction credits and minimal impact on the process. Other NO_x reducing technologies such as SNCR and additives offer different levels of NO_x removal as well as different levels of capital and operating costs. Each refiner must assess the suitability of each technology option with respect to their goals and constraints in an effort to maximize value of capital employed.

Allowances and emissions credits will have a major role in managing NO_x and other pollutant emissions. Credits must be obtained to offset any overproduction of permitted allowances. Allowances decrease over future years to stay in line with the region's environmental goals. Emission credits created by SCRs commissioned prior to April 1, 2004 will recoup most if not all the capital investment for the SCR. ERCs represent a costly option that allows operators permission to exceed their allowances without penalty. Future supply of available emission credits is difficult to forecast in an environment of increasing demand. This uncertainty makes valuation of these credits volatile which has attracted the attention of speculators.

About the Authors

Dennis L. Salbilla joined the DeNO_x Group of Haldor Topsoe Inc. in January to center attention on the refining industry in the U.S. and Canada. Prior to joining Haldor Topsoe, he worked for ExxonMobil as a Business Analyst. His gained exposure to Energy Industry Investment Banking at Raymond James and Associates and Credit Lyonnais Securities while pursuing an MBA. Before returning to graduate school, Salbilla worked for AKZO Nobel and UOP, primarily on Fluid Catalytic Cracking and Resid Catalytic Cracking units.

Salbilla holds a BS in Chemical Engineering from the University of Illinois, Chicago and an MBA with a concentration in Finance from the University of Houston.

Randall Lack began his career as an entrepreneur, starting and selling his first company by the age of 17. He served as the Marketing Coordinator for ProActive Computer Services, and assisted them from the development stages of the corporation through IPO. After working with ProActive, Randall joined ICS-Innovative Solutions, a consulting firm, and served as VP of Business Development. He worked with Dan Sloan, president of ICS-Innovative, and now president of Emission Credit Brokers, in founding Emission Credit Brokers in 2001. Randall now runs the brokerage desk for Emission Credit Brokers, and has used his entrepreneurial and risk management background to leverage his position in the environmental brokerage industry.

He is a Magna Cum Laude graduate from the University of Houston with a B.B.A. and a minor in Asian Studies. Mr. Lack is a member of the Emissions Marketing Association (EMA) and has been appointed to serve on the contracts committee. Randall is Vice President of Memorial-Hermann Prevention and Recovery Center and serves on the Clean Air Action Committee of the Greater Houston Partnership.