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THE ROLE OF ADDITIVES IN REDUCING FLUID CATALYTIC CRACKING SO_X AND NO_X EMISSIONS

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Abstract. *Reduction of SO_x and NO_x from refinery fluid catalytic cracking (FCC) units has become an issue globally. Countries within the European Union have begun to define requirements under the National Emissions Ceiling (NEC) Directive. Countries engaged in the enlargement of the European Union must also meet environmental considerations and therefore clearly have an interest in understanding how to best manage emissions from FCC units.*

The efficiency and effectiveness of emissions reduction additives for SO_X and NO_X continue to improve dramatically allowing refiners to target specific pollutants on an as-needed basis while maintaining operational flexibility. Examples will be provided that highlight the ability to reduce additive test time and cost, allowing refineries to optimize performance will minimizing emissions.

Key words: *additives, environmental regulations, emission control, FCC, Fluid Catalytic Cracker flue gas, hydrotalcite, NEC, Nitrogen, NOx, , pick-up agent, pollution, Spinel, SOx, Sulfur.*

Environmental Regulations Affecting Refiners

There is global concern over the impact of SO_X, NO_X, and CO emissions on our environment. Sulfur oxides are a primary contributor to acid rain and have been shown to cause respiratory problems in cities by promoting the formation of PM_{10} particles. [1] NO_X is a precursor to acid rain as well as being a major contributor to the smog that can blanket large cities. Studies have shown that ozone formation results from a complex set of chemical reactions involving volatile organic compounds (VOC) and NO_X. The reduction of ozone levels is only possible in some cases through the reduction of NO_X [2].

In Europe, the EU Commission has adopted the National Emission Ceiling (NEC) Directive requiring a 77% reduction in SO_2 and a 48% reduction in NO_X by 2010 (1995 basis). [3] Compliance planning on a country by country basis started in October 2002 with a review called for in 2006. Several other Directives like the REC – Regional Environmental Center for Central and Eastern Europe (CEE) in Hungary and SILAC – Sofia Initiative on Local Air Quality report on the progress in reduction of SO_2 and particulate emission in a number of Eastern European Countries, will have an impact on FCC refiners including Integrated Pollution Prevention and Control, and the Air Quality Framework.

It has been argued that refineries, particularly FCC operators, are not the major source of pollutants and are being unfairly targeted. While it is true that mobile sources (vehicles) are much higher contributors to atmospheric pollution than stationary sources, solutions must encompass everything from "well to wheel". Refinery emissions tend to be very concentrated and therefore contribute significantly to localized pollution problems. Refiners will continue to grapple with appropriate strategies to meet the required emission reductions of key pollutants.

Environmental regulations add another set of variables to the already complex trade-off decisions that refiners have to make. One common denominator globally is that FCCU emissions legislation will continue to evolve and refineries with FCCUs need to make the decisions based on their own particular situation. "How will we reduce SO_X emissions if we shift to more sour crudes?" "Should we invest in capital to reduce emissions of SO_X and NO_X or use additives?" "What level of emissions reduction is achievable with each alternative?" "Can we redesign portions of our process to meet projected market demand while maintaining acceptable emissions levels and what are the risks associated with this investment?" These are only a portion of the questions that each company and every individual refinery are forced to ask within a given set of boundary conditions. Complicating these quandaries is the rate of technical advancement made in a variety of competing solutions. There is no single solution. As suppliers we must provide our customers with the information they need to help them make informed decisions.

The Solutions

When looking at means for reducing SO_X emissions from a FCC unit there are at least five potential solutions:

1. Processing of low sulfur feed stocks
2. Feed hydrotreating
3. Flue gas scrubbing
4. Catalytic SO_X control (Additives)
5. Combinations of the above

Each alternative has ramifications beyond the direct environmental impact and each offers advantages and disadvantages, details of which are beyond the scope of this paper.

It is important to consider the financial implications of each solution relative to the others. Every refinery operates under its own set of conditions that affects the applicability of any particular option. It is thus unrealistic to offer up a single solution for everyone. However, we can look at specific previously published examples.

Feed hydrotreating is the most capital intensive solution with cost estimates of fifty to several hundred million dollars.

Flue gas scrubbing has the next highest level of capital investment. Grace Davison published, in March 2000, a comparison of wet gas scrubbing with a catalyst additive and a catalyst additive combined with an ESP. This analysis was comprehensive in that it captured the total capital cost of the scrubber including design, engineering, site preparation, equipment, installation, instrumentation and waste treatment. A financial analysis that included both capital and operating expenses showed that use of a catalyst additive in combination with an ESP was most cost effective is meeting emissions regulations on a basis of dollars per kg of SO_X removed. For the specific FCC unit analyzed, the \$/kg of SO_X removed were 0.79, 0.45, and 0.67 for the scrubber, catalyst additive alone, and catalyst additive plus ESP, respectively. [4] Although an additive alone appears to be the least expensive option, the decision must comprehend the permitted emissions levels that can vary depending upon the solution.

Belco Technologies Corporation has published several papers promoting the use of wet gas scrubbers to control SO_X flue gas emissions. The flexibility of their proposed scheme allows for particulate-only removal followed by a later addition of SO_2 removal. Several alternative technologies are discussed and equivalent costs, in \$/ton SO_2 removed, are provided. It is unclear if and how capital has been factored into the calculations, but values from about \$0.44 to \$0.70 per kilogram of SO_2 removed are achieved with their caustic scrubber, soda ash scrubber, soda ash scrubber with crystallizer and regenerative scrubber solutions. [5]

An additive-only solution is generally the least expensive when the total system cost, including both capital and operating expenses, are included. However, this may not be true for systems requiring extremely high additive additions where both dilution and opacity issues can become concerns. Advances in SO_X reduction additives solve these problems and will be discussed in detail later.

The Benefits of an Additive Solution

The FCC has always been viewed as a flexible process. Adjustments can be made to product slates, operating conditions and feedstocks. Additives, which have been used since the 1970s, are one of the primary ways to minimize the environmental impact of FCC units. They provide advantages not always available through alternatives including their relative ease of use and their relatively quick effects (instantaneously for CO promoters and NO_x reduction additives to hours or days for SO_X reduction additives depending on the base load). [6 ,7]

Additives offer flexibility that is not possible with fresh catalyst additions which require a complete inventory change out. This may not be viable given seasonal changes or when other operating objectives change only slightly. The practice of blending of emissions reduction additives with the base catalyst can cause some problems. When CO promoter is blended with the fresh catalyst, optimization may not occur. Situations have occurred where over promotion resulted in increased formation of NO_x emissions.

In today's environment, the ability to respond quickly and with relative ease has made additives a mainstay for refiners wanting greater flexibility. Examples include allowing use of sour crude oils or when a backup to SO_X control is required during a hydrotreater shutdown. Additives have recently been used to meet environmental legislation on SO_X emissions. Their flexibility can provide a balancing mechanism in meeting both local and national emissions regulations.

The use of specialized addition systems has made additive usage extremely cost effective. The cost of additives is generally high compared to fresh catalyst. It is therefore critical to add only what is required to meet the intended purpose. INTERCAT provides addition systems that offer their customers the flexibility required from additives.

SO_X Reduction Additives

Developed in the late 1970s SO_X reduction catalysts were initially alumina based. [11] While these were shown to be effective when promoted with rare earths, especially cerium, they were shown to be particularly susceptible to deactivation. The deactivation was difficult to prevent but was partially offset by the use of high capacity materials. These catalysts were shown to differ in both sorption activity and the extent to which they released sulfur under reactor conditions. Their commercial application was dependent upon regenerator temperature, reactor conditions, and the fresh catalyst they were used with. [8] Although this additive removed SO_X, its' effectiveness was reduced due to the limited sorption capacity.

The first technology to offer an alternative was a magnesium aluminate spinel-based technology [9] that has been further advanced and is still offered today. Spinel technology was originally developed by ARCO in the 1970s with advancements in the use of magnesium for SO_3 pick-up made until the late 1980s. This type of product has remained essentially unchanged since the early 1990s.

Realizing the importance and effectiveness of the magnesium species in the sorption of SO_X, in the late 1980s, Akzo Nobel patented the use of hydrotalcite and related compounds for use in an FCC to reduce SO_X emissions. The importance of hydrotalcite and hydrotalcite-like compounds is they potentially contain more active Mg species than spinel. Hydrotalcite based compounds typically contain 3-4 moles of Mg per mole of Al while spinels contain 1 mole of Mg per 2 moles of Al. This difference translates into improved product performance.

Unfortunately, early hydrotalcite technology required it to be supported or otherwise bound resulting in less than optimal performance. In 1997, INTERCAT developed and patented a self-supporting hydrotalcite that overcame previous technology barriers. The resulting product was named SOXGETTER™.

SO_X reduction additives remove SO_X from the regenerator flue gas and release the sulfur as H_2S in the FCC reactor. The amount of SO_2 removed is almost directly proportional to the amount of additive used. It is also dependent on the excess O_2 level in the regenerator. Normal additive levels in the catalyst inventory range from 1 – 10% and typical SO_X removal rates are 20 – 60%, but rates in excess of 90% have been achieved.

SO_X reduction catalysts are basically two component systems. The first component oxidizes SO_2 to SO_3 in the regenerator.

$$SO_2 + ½\,O_2 \rightarrow SO_3 \qquad (1)$$

The second component, commonly referred to as the "pick-up agent", removes the SO_3 from the regenerator as a metal-sulfate and releases it as H_2S in the reactor or stripper. Both components of the additive must work together for maximum SO_X removal. Magnesium-based materials are used in currently available additives. The additive reacts with SO_3 to form magnesium-sulfate. Once the additive has picked-up SO_3, it circulates with the catalyst to the reactor. In the reducing environment of the reactor, at least a portion of the hydrogen sulfide is released and the additive reverts to its original state.

$$MgO + SO_3 \rightarrow MgSO_4 \qquad (2)$$

$$MgSO_4 + 4H_2 \rightarrow MgO + H_2S + 3H_20 \qquad (3)$$

The H_2S then exits the FCCU in the dry gas and is then removed by the sulfur recovery unit. This increase in H_2S, 5-20%, can typically be managed within a refinery's operations.

The following is a summary of factors affecting SO_X reduction additive efficiency:

- Feed quality is the most significant factor. The sulfur content and particular species present in the feed strongly determine the extent of potential SO_X emissions. Typically 10% of the sulfur in feed goes to SO_X, but it can vary from 5 to 30 wt%.
- FCC catalyst also plays a role in reducing SO_X emissions. The active alumina in FCC catalysts can act as a "pick-up" agent for SO_3 (similarly to MgO). What fresh catalyst lacks are the oxidants that enhance the effectiveness of SO_X reduction additives.
- The presence of CO promoter catalyses the oxidation of SO_2 to SO_3 and therefore enhances the SO_X removal process. Higher concentrations of SO_3 are also produced in the presence of excess oxygen, so SO_X reduction additives tend to be more effective in full combustion regenerators.
- Increasing catalyst circulation rate increases the availability of fresh metal oxides for SO_3 pick-up and hence reduces SO_X emissions.
- Lower regenerator temperatures tend to favor SO_3 formation, while a good air distribution and mixing in the regenerator enhances SO_3 pick-up.
- Large regenerator inventories will reduce the efficiency of an additive, and inefficient strippers increase the amount of sulfur going to the regenerator, and hence the SO_X emissions. [10]

The understanding of SO_X reduction additives continues to grow and with it advancements in both the efficiency of additives and the degree of technical service available from suppliers. The higher contained MgO in SOXGETTER compared to DESOX® has translated into equivalent or better commercial performance (Table 1) [10].

Since the commercial launch of INTERCAT's hydrotalcite containing additive, SOXGETTER™, there has been a continuing evolution in the performance of this product family. The level of contained MgO in SOXGETTER has recently been increased at the expense of the structural hydroxyls in the hy-

Table 1. Commercial Results of SO_X Reduction Additives

FCC Unit Type	**Kellogg**		**UOP High Eff. Reg.**		**UOP SBS**		**UOP Stacked**
Combustion Mode	**Total**		**Total**		**Total**		**Partial**
Additive	*SOXGETTER*	*DESOX®*	*SOXGETTER*	*DESOX®*	*SOXGETTER*	*DESOX®*	*SOXGETTER*
Feed Quality							
Fresh Feed Rate, MBPD	19.1	18.5	55.5	53.6	64.0	63.0	7.0
Fresh Feed API	24.2	24.7	23.2	22.7	21.1	21.2	26.3
Fresh Feed Sulfur, wt%	0.52	0.54	0.71	0.70	1.25	1.49	0.55
DCO Sulfur, wt%	1.25	1.22	2.26	2.12	2.86	3.37	1.45
Operating Conditions							
Reactor Temperature, °F	1009	1009	1006	999	1005	1005	985
Regenerator Dense T, °F	1323	1325	1368	1369	1357	1362	1270
Regenerator O_2, vol%	1.9	1.9	0.9	1.1	1.1	1.3	1.5
E-cat Ni, ppm	1800	1700	500	500	2600	2600	1900
E-cat V, ppm	2800	2600	1960	1960	3000	3000	900
Additive Addition, lb/day	728	676	1583	2081	2125	3240	40
Emissions							
Uncontrolled SO_X, lb/hr	1181	1086	2046	1895	3100	3853	35
Controlled SO_X, lb/hr	154	141	286	303	868	1117	11
Controlled SO_X, ppmv	188	179	358	370	575	754	98
Reduction, %	87	87	86	84	72	71	70
Additive Efficiency, lb/lb at equivalent SO_X reduction level	**34**	**34**	**27**	**18**	**25**	**20**	**15**

Table 2. Commercial Comparison between SOXGETTER and Super SOXGETTER

	SOXGETTER	**Super SOXGETTER**
Feed Quality		
Fresh Feed Rate, MBPD	54.4	54.4
Fresh Feed API	30.3	30.3
Fresh Feed Sulfur, wt%	0.42	0.40
DCO Sulfur, wt%	1.41	1.34
Operating Conditions		
Reactor Temperature, oF	1011	1007
Regenerator Dense T, oF	1278	1278
Regenerator O_2, vol%	3.5	3.4
Ecat Ni, ppm	897	1095
Ecat V, ppm	2037	2281
Additive Addition, lb/day	233.7	137.9
Emissions		
Uncontrolled SO_X, lb/hr	314	306
Controlled SO_X, lb/hr	164	147
Controlled SO_X, ppmv	148	133
Reduction, %	48	52
Additive Efficiency, lb/lb at equivalent SO_X reduction level	**16**	**29**

drotalcite, without any degradation in physical properties, resulting in the development of Super SOXGETTER. Table 3 shows a direct comparison of SOXGETTER and Super SOXGETTER efficiency from a carefully run trial using average SOXGETTER efficiency as the baseline. In this comparison, Super SOXGETTER demonstrated an 80% increase in SO_X reduction efficiency.

What is clear is that the efficiency of SO_X reduction catalysts has improved and continues to improve dramatically with time. Increases in efficiency like that exhibited by Super SOXGETTER relative to SOXGETTER allow refiners with dilution issues to avoid them.

In most cases, SO_X reduction catalysts can cost effectively meet emissions regulations. Commercial SOXGETTER data have shown that an 85% reduction in SO_X removal, resulting in 50 ppmv emissions, can be achieved with an efficiency of 18 pounds SO_X per pound of additive. Decreasing emissions to below 25 ppmv reduced the additive efficiency to below 14 pounds SO_X per pound of additive. The concentration of SOXGETTER required to reduce emissions below 25 ppmv was slightly greater than 5 weight percent of the total catalyst inventory. The relative cost increase to reduce emissions from 50 to 25 ppmv was 31%. Each unit must be analyzed to understand the shape of performance efficiency curve for their unit and compare it with the alternatives available.

When using a SO_X reduction additive, the most effective way to introduce it into the FCC unit is through regular, small charges. This can be achieved using INTERCAT's patented additive addition systems that have proven to be reliable and very accurate tools. The effective use of an addition system with SO_X reduction catalyst was proven at a U.S. refinery. Two products were used during two different time periods. For the first time period each product was added as needed typically one to four times a day. For the second time period an INTERCAT additive addition system was used to regularly add a small amount of additive every few minutes. Table 3 provides details of the testing.

Table 3. Comparison of SO_X Reduction with and Without Addition System Usage

Period / Product	**Uncontrolled SO_2** (Lb/hr)	**Controlled SO_2** (Lb/hr)	**SO_2 Removed** (Lb/hr)	**Additive Usage** (Lb/day)	**Additive Efficiency** (LB / Lb)	**SO_2 Reduction** (%)
Period #1 – 7 months (no addition system)						
Product 1	388	251	137	242	14	35
Product 2	502	295	207	337	15	41
Product 1	462	274	187	265	17	41
Period #2 – 4 months (INTERCAT addition system						
Product 2	580	267	313	176	43	54
Product 1	608	278	331	173	46	54

Table 4 shows that calculating total SO_2 removed and total additive over the two entire trial periods shows the additive efficiency using the INTERCAT addition system is three times greater than without it. A conclusion to this study is that adding small amounts frequently can give large gains in additive efficiency and cut additive costs significantly.

Table 4. Total Efficiency of SO_X Reduction Catalyst (Including both products shown in Table 5)

Period	Controlled SO_2 (ppmv)	Additive Efficiency (Lb/Lb)
Period #1 – 7 months (no addition system)	206	13.9
Period #2 – 4 months (INTERCAT addition system)	220	41.8

NO_X Reduction Additives

NO_X reduction additives, originally introduced in the mid-1990s, are the latest additions to FCC additives. [11 , 12] Most early published literature on FFCU NO_x reduction focused primarily on three major areas: the sources of nitrogen, reactions involving various nitrogen containing species within the FCC unit, and potential ways of reducing NO_x emissions. Despite an apparent understanding, translating additive findings in non-commercial trials to commercial success on FCCUs has shown limited success. Today, some of the same questions remain, however a great deal more trial data have been published. [4, 13] Unit specific operating variables are being modeled to help better understand NO_X emissions behavior [14].

INTERCAT has devoted significant research and development effort to this area, in order to remain at the forefront of NO_X additive development. It has become clear through this effort that the reduction of NO_X from the FCC is a complex process with many interdependencies. There are three major sources of nitrogen in the FCC regenerator: nitrogen compounds in coke that result from the feed, nitrogen from air in the regenerator, and nitrogen from the combustion air to CO boilers in partial burn units. A strong dependence has been observed in all trials between NO_X and excess O_2 in the flue gas. A poor distribution of O_2 in the regenerator bed can result in large variations of NO_X on a local scale. Competition between other gaseous species present in the regenerator can also affect NO_X levels. This implies that manipulation of the NO_X: O_2 relationship is crucial to reducing NO_X from the FCC unit.

There appears to be no direct relationship between feed nitrogen and NO_X emissions (Figure 1).

The strong relationship between excess oxygen and NO_X emissions was also confirmed (Figure 2). In order to effectively manage NO_X there is a need to reduce excess oxygen, but ensure combustion and allow regeneration of the catalyst.

INTERCAT has developed and commercialized a family of NO_X reduction additives called NOXGETTER™ technologies. NOXGETTER Types A and B are products that capitalize on the inherent gradients that exist in the regenerator atmosphere.

NOXGETTER Type A has reduced NO_X emission by 60% in commercial trials at Refinery A (Figure 3).

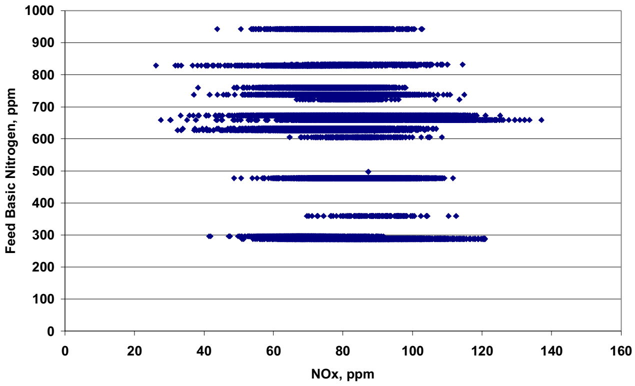

Figure 1. Relationship between Feed Nitrogen and NO_X Emissions

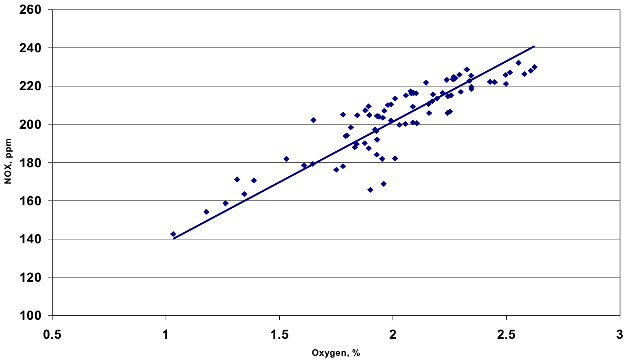

Figure 2. Relationship Between Excess O_2 Additions and NO_X emissions

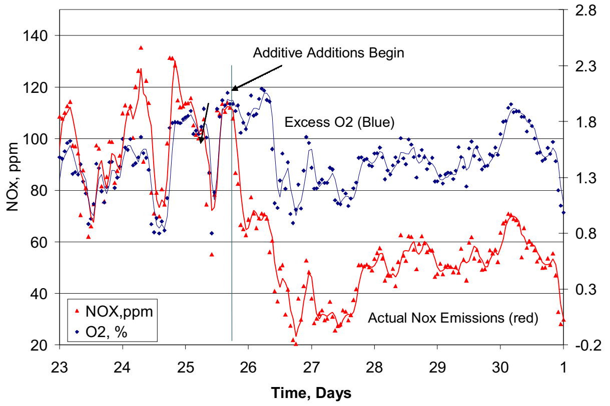

Figure 3. Comparison of Actual and Predicted NO_X emissions

Figure 4 and Figure 5 show the clear relationship between oxygen levels and NO_X emissions over three days and one month, respectively.

A second trial at Refinery B (Figure 6) shows only a 30% reduction demonstrating the unit specific nature of NO_X emissions.

NOXGETTER Type B has been used commercially to reduce NO_X emissions by 40-50% with as little as 0.1% in the total catalyst inventory (Figures 7). Larger reductions are possible at higher additive concentrations; however, each unit needs to be optimized for its' particular cost: NO_X reduction curve.

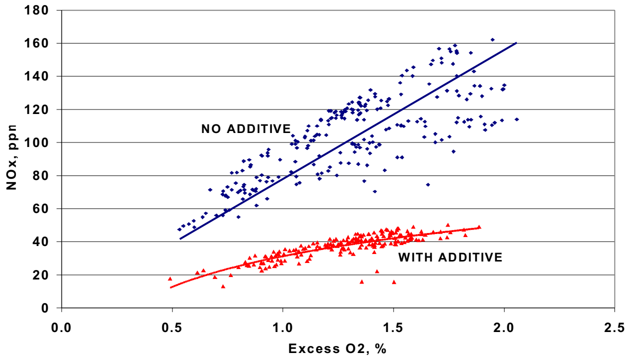

Figure 4. Refinery A: Relationship Between Oxygen Additions and NO_X emissions (3 day period)

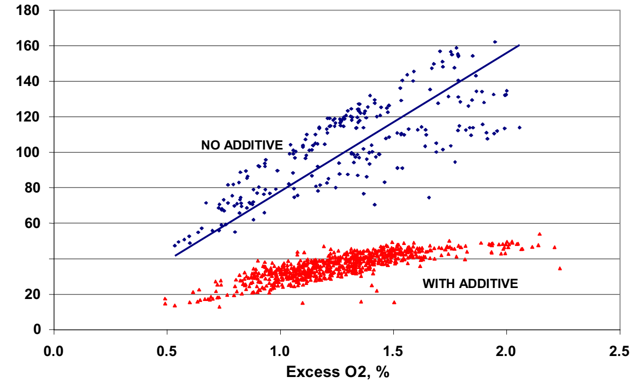

Figure 5. Refinery A: Comparison of Actual and Predicted NO_X emissions (1 month period)

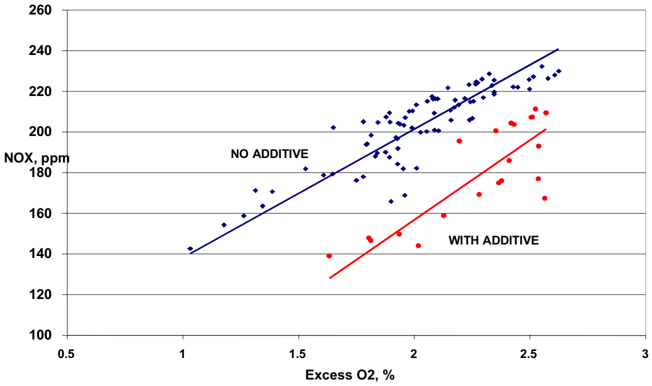

Figure 6. Refinery B: Relationship Between Oxygen Additions and NO_X emissions

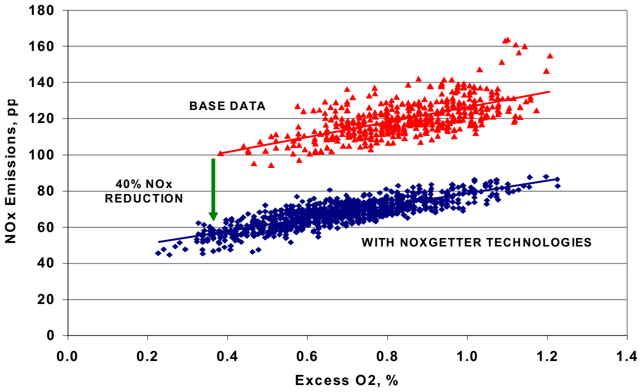

Figure 7. NO_X Emissions as a Function of Excess O_2 at Refinery C

In the United States, so called consent decrees covering NO_X emissions from FCCUs are being negotiated or in some cases have already been signed. In some cases there is a demonstration period that allows several options to be evaluated in order to understand both the capability of various technologies and cost to implement various levels of emissions reductions. Consent degrees have been issued with goals of $10,000 per ton of NO_X removed. It is not uncommon for testing of catalytic additives at 2 weight percent of inventory. It is INTERCAT's experience that these high addition levels may not be required, and may even deter their performance. As an example, INTERCAT's NO_X reduction additives have reduced NOx levels by up to 60% with additions at the 0.5 weight percent level.

INTERCAT's experience with NO_X reduction additives continues to mature. Commercial testing combined with research and development efforts confirm that there is no single additive solution for all FCC units. The reduction of NO_X from the FCC is a very complex process with many interdependencies. NOXGETTER technologies have shown NO_X emissions reduction greater than 50% with additions of less than 1% of inventory. FCC units can be assessed in a few days with an optimization period required to maximize cost effectiveness for a particular NOx reduction requirement.

Summary

For more than thirty years, catalyst additives have been used in FCC units, to improve their performance and reduce unwanted emissions. While some products have remained unchanged for decades, new products and enhancements to existing additives continue to improve their cost effectiveness. Advances continue to extend the usefulness of additives in delivering cost effective solutions to CO, NO_X, and SO_X emissions and to meet environmental legislation globally. The complex interdependencies that exist between catalyst additives and the unit specific nature of FCC units require a comprehensive understanding of the chemistry, operating parameters, and overall refinery strategy. Only by working together, can refiners and suppliers develop the most effective solutions.

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