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SOx Reduction at a European Refinery

A trial run of a new SOx reduction additive preblended with catalyst in a full burn FCC unit yielded significant savings when compared to current costs of rare earth based SOx reduction additives

Maria Luisa Sargenti, Grace Davison

Many FCC operators use SOx reduction additives to provide a fast, no-capital approach for controlling SOx emissions. For this objective, the low rare earth Super DESOX® additives from Grace Davison contain a high amount of cerium (Ce) to promote the oxidation reaction of SO_2 to SO_3, forming the metal-SO_4 on the additive surface. In an effort to minimize the impact of the global rare earth (RE) situation on the economics of SOx controlling additives, Grace is offering refiners the opportunity for a trial run with the Grace Davison SOX MCD. This newly developed additive has been designed to be a cost/effective solution to reducing SOx emissions in FCC flue gas.

The amount of RE in SOX MCD has been optimized and better distributed in order to preserve as much as possible Super DESOX ® performance. In this instance, an FCC unit described in **Table 1** at a refinery in Western Europe benefitted from an SOX MCD trial run. Since 2008, efforts had begun at this facility to seek SOx emissions control alternatives.

In the trial run, uncontrolled emissions were measured with continuous emissions monitoring systems (CEMS) gas analyzers. A base line correlation was selected for calculating uncontrolled SOx prior to Super DESOX® addition with the FCC catalyst noted in Table 1. In this trial, MgO in e-cat was monitored along with SOx emissions in the flue gas. Actually, the desired 30% SOx reduction was achieved with only 0.5 wt% Super DESOX®.

Super DESOX® has been used on a regular basis since 2009. For an easier operation the additive has been supplied preblended with the catalyst. After the 2011 turnaround the refinery switched directly from Super DESOX® to SOX MCD. Since then, SOx control additive has been on a continuous usage. The same SOx base line (correlation) developed in 2008 has been used for the performance evaluation. At the current additive level, the SOX MCD is

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Table 1. FCC unit description.

FCCU design	Kellogg Orthoflow
FCCU catalyst inventory	110 MT
Fresh catalyst addition rate	5 MT/day
Catalyst	NEKTOR-ULCC promoted
Operating mode	Full burn
Regenerator temperature	`Typically ~ 730°C
Excess O2	Typically ~ 2-3%
Sulfur in feed	typically 0.3 to 0.5%
Uncontrolled SOx	Around 1000 mg/Nm3

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outperforming Super DESOX® (**Figure 1**).

Factors affecting additive performance must be accounted for (**Table 2**), including:

- Sulfur content in feed, which increases SOx available for removal
- Oxygen content in the regenerator dense phase, which drives oxidation of SO_2 to SO_3 (often the rate limiting step)
- Regenerator air distribution (good contact between additive and SOx improves kinetics)
- Catalyst circulation rate (performance is proportional to circulation rate)
- Stripping efficiency (improves regeneration of the SOx control additive)
- Regenerator temperature (Negatively affects the SO_2 to SO_3 reaction).

Cost Effective Alternative

In the past Super DESOX® has proven to be efficient in removing SOx under diverse operating conditions. A higher dosage of SOX MCD might be required to match the performance of Super DESOX®. The experience in full burn FCC regenerators is showing that 20-25% more SOX MCD is required. Nevertheless, after the commercial trials performed in today's high rare earth cost environment, SOX MCD is the most cost effective alternative for SOx control in the FCCU. ■

Editor's Note: This article was based on a presentation by Maria Luisa Sargenti (maria.sargenti@grace.com) at the Grace Davison Symposium in Munich, Germany (September 2011) and was based on data generated at European refinery up to July 30, 2011. At press time, the SOX MCD additive is available to refiners for further trials.

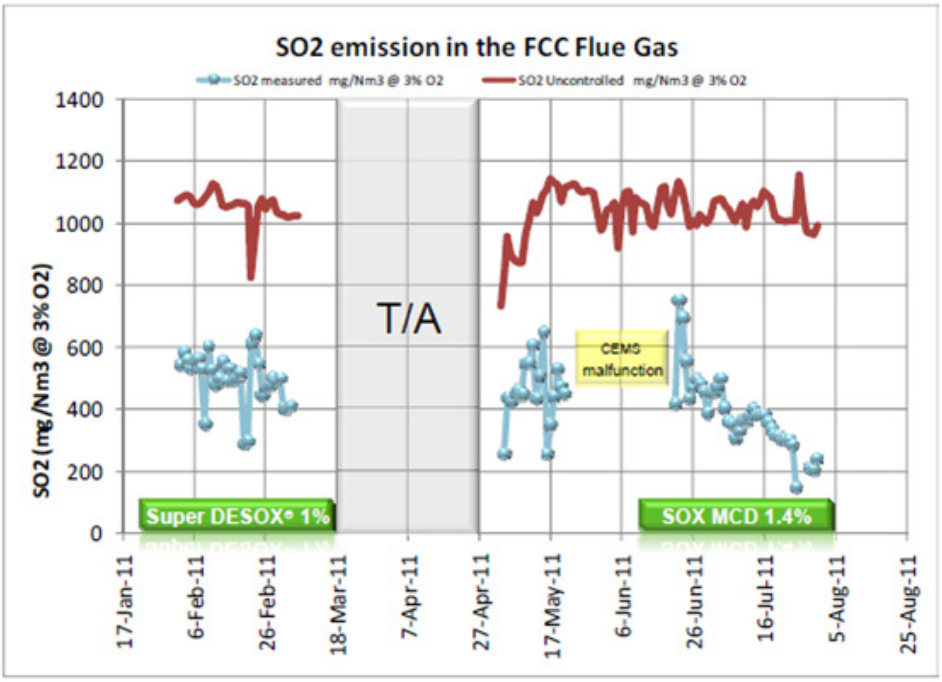

Figure 1. SOX MCD trial at European refinery.

Table 2. Key facts during additive trials.

Trialed Additive:	Super DESOX®	SOX MCD
Uncontrolled SOx	1030 mg/Nm^3	1075 mg/Nm^3
% Sulfur in feed	0.40 wt%	0.41 wt%
% Additive in CAR	1.00%	1.40%
Feed rate	`185 MT/h	152 MT/h
C/O	4.9	5.2
CAR	5 MT/day	5 MT/day
Regen temperature	729 °C	726 °C
Daily inventory replacement	4.50%	4.50%
SOx reduction	50%	66%
PUF	30	23
Savings on additive costs* * considering RE prices @ 3Q2011	---	200,000 EUR/yr (-40%)

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INDUSTRY NEWS

Rabigh Phase II Project Expected to Begin Operations in 2016

Saudi Aramco, together with its partner Sumitomo Chemical, have made significant progress on the feasibility of the Rabigh Phase II Project and will proceed to implement the expansion of a world-class petrochemical complex on the Kingdom's west coast as reported in the *MENAFN* Arab News on May 26.

Rabigh II will complement Saudi Aramco's existing petrochemical investment in the Rabigh I petroleum refining and petrochemical production complex, currently owned by Rabigh Refining and Petrochemical Company (PetroRabigh), a joint stock company initially founded by Saudi Aramco and Sumitomo Chemical.

The Rabigh II feasibility study and front-end engineering (FEED) design work were jointly undertaken and funded by Saudi Aramco and Sumitomo. As part of the next phase implementation of Rabigh II, Saudi Aramco and Sumitomo Chemical are finalizing various project milestones, including contracts for engineering, procurement and construction and other project-related agreements, as well as project financing.

Rabigh II's development will include a new aromatics complex and an expanded facility to process 30 million standard cubic feet per day of ethane and approximately 3.0 million tons per year of naphtha as feedstock to produce a variety of high value-added petrochemical products. The total project investment is currently projected to reach approximately $7 billion.

The project is expected to begin operations in the first half of 2016. It is envisaged that PetroRabigh will be approached in due time and presented with the opportunity to serve as the project company for Rabigh II subject to PetroRabigh's independent evaluation of the project feasibility results and separate corporate and regulatory approval procedure.

Rabigh II's main products will be ethylene propylene rubber, thermoplastic polyolefin, methyl methacrylate monomer, polymethyl methacrylate, low density polyethylene/ ethylene vinyl acetate, para-xylene/benzene, cumene and phenol/acetone. Additionally, Saudi Aramco and Sumitomo Chemical will continue to implement other product lines on optimal schemes to realize further project optimization. ■

Shaw Selling E&C Division to Technip

Shaw Group Inc announced May 22 that is selling its energy and chemical (E&C) division to Technip for $300 million, this includes FCC and ethylene technology capabilities. Shaw said it would retain E&C staff in its Baton Rouge office as well as a consulting unit, and both would be moved into other divisions. Shaw will also retain its Toronto office, as well as obligations related to a nearly complete ethylene plant in southeast Asia. Technip said Shaw would also retain all legacy engineering, procurement and construction contracts. Technip said the "downstream" technology it was buying from Shaw complemented its work in energy production. "In addition, we gain access to promising growth areas, including U.S. petrochemical investments driven by low-price shale gas," CEO Thierry Pilenko said in a statement. The purchase from Shaw should be done by the end of its fiscal year in August, said Shaw. ■

Sinopec Examining Business Case for South African Refinery

A May 22 report in *EnergyChinaForum.com* noted that South African national oil company PetroSA said it had partnered with China's Sinopec group to push along the building of its Coega refinery, originally slated to cost $9-$10 billion and produce 400,000 bpd. The Mthombo project, in the industrial port of Coega near Port Elizabeth on South Africa's south coast, has been under consideration for several years but progress has stalled mainly because of a lack of funding.

The agreement defines the process by which PetroSA and Sinopec will shape the business case for Project Mthombo, the initiative to construct a world-class crude oil refinery at Port Elizabeth's Coega Industrial Development Zone," PetroSA said. The first phase of the agreement will focus on building a business case for the plant, and the second will consider engineering and design, it added. Sinopec is expected to complete both studies over the next 18 months. China has set aside $20 billion to invest in South Africa's energy sector, part of its growing presence on the continent. ■

PetroChina to Begin Construction of New Refinery

C1 Energy noted on May 23 that PetroChina is planning to begin construction on a $3.0 billion crude refining project in Anning, Yunnan, China, in the second half of 2012. Designed to process sour crude including oil and gases from the Middle East, the refining project involves construction of a 10 million tonnes per annum crude distillation unit; a 3.6 million tonnes per annum residue hydrogenation unit; a 3.0 million tonnes per annum FCC unit; a 2.0 million tonnes per annum reformer; a 1.8million tonnes per annum hydrocracker and a 1.0 million tonnes per annum naphtha cracker. The company had a total of 12.2 million tonnes per annum of refining capacity in southwest China at the end of 2011, according to ICIS C1 data. The refining capacity in the region is likely to reach 32.2 million tonnes per annum by the end of China's twelfth five-year plan period (2011-2016), representing 12% of PetroChina's total capacity. The refining project is expected to be completed in 2014. ■

Middle Eastern Refiners Exerting Downward Pressure on European Refiners

A May 23 report from *Dow Jones newswires* noted that an Eni SpA executive explained that a refining boom in the Middle East is putting pressure on European refiners because the MidEast producers, who have lower costs, are now entering the market in Europe, especially the Mediterranean.

"Italy was a hub for Middle Eastern crude, but not anymore as Middle East [oil companies] are now vertically integrated," Domenico Elefante, Eni's executive vice president for refining, told *Dow Jones Newswires* on the sidelines of the Global Refining Summit in Barcelona. The report noted that Eni is mainly sourcing oil from West Africa, the Middle East, Russia and Venezuela. Elefante also said output at Eni's Sicilian refinery of Gela had already fallen sharply amid a one-year partial shutdown announced last month. Refinery runs at Gela will fall by more than 60% by the middle of June to about 30,000 bpd compared with levels seen before the partial shutdown. ■

Jamnagar Refinery Gasification Plant will Provide Petrochemical Feedstocks

Reliance Industries Ltd announced May 22 that it has selected Philips 66's E Gas Technology for its planned gasification plants at Jamnagar which is the largest refining complex in the world with an aggregate refining capacity of 1.3 million bpd. By using the E Gas Technology, the planned gasification plants at Jamnagar will be among the largest in the world and will process petroleum coke and coal into synthesis gas. The synthesis gas will

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be used as feedstock for a new chemical complex and will fuel the refinery s existing gas turbine power generation units.

Phillips 66 will license its E Gas&trade Technology to Reliance and provide process engineering design and technical support relating to the gasification technology process area.The E Gas&trade Technology has been utilized in commercial applications since 1987. It incorporates a gasification system design that can be applied with gas and steam turbine combined cycle power generation to produce electric power as well as synthesis gas applications for the production of hydrogen chemicals or substitute natural gas in highly flexible combinations. ■

Valero Acquires HF Alkylation Safety Monitoring Technology

Invensys Operations Management announced May 23 that it has signed a multi-year licensing agreement with Valero Energy Corporation, allowing use of Invensys Operations Management's patented ACA.HF Advanced Alkylation Measurement Solution. In the first phase, Valero will implement the solution at seven refineries globally. The Invensys solution monitors and measures hydrofluoric (HF) acid levels in real time by analyzing differential responses from online sensors, helping to improve the safety, reliability and environmental performance of the refinery and creating new opportunities to reduce operating costs.

Commonly used in petroleum processing, HF acid is a highly toxic catalyst that must be carefully managed and controlled. Accurately analyzing how much HF is re-circulating within the process contributes significantly to increasing the efficiency of the refinery because it can improve crude stock yield and associated costs. Early approaches to HF monitoring involved taking manual samples and analyzing them in a laboratory. This approach however, even when carefully executed, potentially exposed lab workers to severe toxins, and its accuracy was limited. And while more recent techniques can produce more accurate readings, their adaptation for real-time online monitoring is complex and costly. ■

Low Rare Earth FCC Catalysts Benefiting Refinery Operations

Low and zero rare earth FCC catalysts for maximizing residue conversion and feedstock flexibility in refinery operations have been of keen interest to many refiners due to the continued volatility of the rare earth market. Wormsbecher et al wrote in the 2010 issue of *Catalagram*® (issue #108) that "rare earth elements perform two critical roles in the FCC catalyst. First, they control the activity, coke selectivity, and olefin selectivity of the zeolite portion of the catalyst. Second, in units that run high vanadium and consequently suffer from severe deactivation conditions, rare earths are used as vanadium traps, improving the coke selectivity even more and also improving the activity retention of the catalyst."

Thus far, a range of zero and low rare earth catalyst formulations have been developed by catalyst suppliers to mitigate the loss of rare earth's benefit to zeolite functionality, which is why development of low and zero rare earth FCC catalysts were discussed in detail at the 6th Annual Global Refining Summit in Barcelona, Spain (May 21-23). For example, one presentation by Colin Baillie, Marketing Manager, Grace Davison Germany, discussed the REpLaCeR™ family of catalysts, of which there are over 50 applications globally. According to the most recent information available from Grace Davison, the REpLaCeR™ family includes five new catalysts for both hydrotreated and resid feed processing with zero and low rare earth content. The REpLaCeR™ family of catalysts utilizes proprietary zeolites and stabilization methods to deliver performance similar to current rare earth-based FCC technologies. ■

EDITORIALLY SPEAKING

The Relevance of Opportunity Crudes Conferences

Rene Gonzalez, Editor
Refinery Operations

The *Hydrocarbon Publishing* Opportunity Crudes Conference held in Houston in early May was well attended by delegates from throughout the world. Refiners in attendance discussed processing and operational challenges encountered in just the past 18 months. To be sure, while there have recently been numerous so called "opportunity crude" forums, it is behooving how many of the opportunity crude process challenges voiced by the delegates have only recently begun to surface.

Because of the surprises refiners are encountering with higher volumes of new crudes, important projects such as converting a ULSD hydrotreater to mild hydrocracking service must be re-examined against a backdrop of feedstock incompatibility issues. No worries! According to some of the technology suppliers in attendance, the onus is on pushing more of these opportunity crude combinations through new or repurposed hydrotreaters and hydrocrackers since hydrogen is currently so cheap.

Regardless of the problems encountered with combinations of heavy feed contaminants (e.g., Ni, N, Na, V, etc.), there is a site-specific solution for every FCC/HDT configuration where opportunity crudes are being introduced. Considering the investment and changes required at the refinery's front end (desalter and crude/vacuum unit), existing downstream thermal and catalytic conversion processes can effectively be operated to meet market objectives, once these feedstock incompatibilities are resolved. For example, BASF's Joe McLean noted in his presentation on resid FCC catalysts that one refinery in Utah reduced FCC unit bottoms yield from 10% down to 5% using the proprietary Stamina™ FCC catalyst. Moreover, cutting bottoms yield in half with the help of this catalyst system was achieved without a coke selectivity penalty, according to McLean. In similar cases, other refiners are looking for ways to increase FCC unit middle distillate (e.g., light LCO) yield without incurring higher bottoms yield penalties.

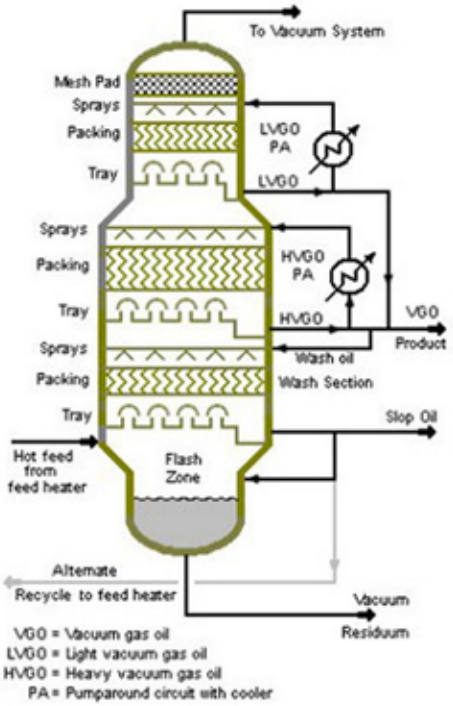

Figure 1. Opportunity crude processing profitability depends on when are where to expect corrosion and fouling in the refinery, including the crude/vacuum tower and linked process assets.

Almost every speaker at the conference was compelled to mention "incompatibility issues," which has become a cliché in the opportunity crude market. Just what type of incompatibilities to expect is key to making an additional $10 to $15/bbl (or higher) if the refiner quickly adjusts treating programs. For example, Nalco's Sam Lordo noted that Bakken crude API gravity varies from 40 to 50, depending on where they are pulling it from. These crudes will lower interfacial tension when blended with asphaltenic crudes. Desalter operations must be carefully adjusted according to Lordo to control potential problems such as overhead corrosion, heater fouling (both organic and inorganic based fouling), etc. Other problems with these opportunity crudes, such as when combined with WCS, Eagle Ford and others, are a result of their high lead content, volatile phosphorous and other contaminants (currently being evaluated).

Other shales, like Niobrara (sounds familiar?) are just now coming to play, so it is perhaps still too early to ascertain how to adjust treating programs when dealing with these emerging feedstocks. As a matter of fact, what to call these hydrocarbons is still a matter of debate. For example, conference delegates noted that Eagle Ford Shale is not really 'shale oil. Rather, it is tight oil (gas and oil tightly trapped in rock). Nonetheless, these shale oils, tight oils and other relatively high API gravity crudes (e.g., condensate crude > 45°API) are backing out the synthetic crudes --- the "original" opportunity crudes that were heavily reviewed five years ago. At the end of the conference, it became quite clear that we are seeing a significant shift in many refiners' overall crude slate. This is not just a North American phenomena, crudes are changing around the world. So, how refiners evaluate these new crude slates within the context of the overall refining economics is why these opportunity crude conferences continue to be relevant.

Refinery Operations wishes to extend their gratitude to *Hydrocarbon Publishing's* president Tom Yeung (tyeung@hydrocarbonpublishing.com) and all his staff for their graciousness in allowing us to report on the conference. ■

Calendar of Events

JUNE

20-21, *Petrochemical Asia 2012*, World Refining Association, Bangkok, Thailand, +65 6590 3972, mustafah@clarionevents.asia, www.wraconferences.com

21-22, *Platts 9th Annual Bunker & Residual Fuel Oil Conference*, Platts, Houston, Texas, USA, +1 866 355 2930, www.bunkerfuel.platts.com

SEPTEMBER

17, *Asia Refining Congress*, Terrapinn Pte Ltd, Singapore, +65 6222 8550, www.tarrapinn.com.

Sept. 30 – Oct. 3, *Middle East Chemical Week 2012*, World Refining Association, Manama, Bahrain, +971 2 401 2929, c.pallen@theenergyexchange.co.uk, www.wraconferences.com

AUGUST

21-22, *AFPM Cat Cracker Seminar*, AFPM, Houston, Texas, USA, +1 202 457 0480, www.afpm.org

OCTOBER

1-3, *AFPM Q&A and Technology Forum*, AFPM, Salt Lake City, Utah, USA, +1 202 457 0480, www.afpm.org

16-18, *Central & Eastern European Refining & Petrochemicals*, 15th Annual Meeting, Bucharest, Romania, +44 (0)207 384 8027, m.altun@theenergyexchange.co.uk, www.wraconferencs.com

22-23, *4th Annual World Refining Technology Summit 2012*, Cerebral Business, Brussels, Belgium, +91 954 099 1011, www.cerebralbusiness.com/wrts