



ADDITIVE INNOVATION

Melissa Clough and Kitty Cha, BASF Corp., USA, demonstrate the benefits of applying SO_x reduction additives for regulatory compliance, with reference to three refinery case studies.

Oil refinery concern over sulfur oxides (SO_x) emissions is steadily present. SO_x emissions cause damage to both the environment through acid rain and to human health by inhalation. In the US, SO_x emissions are regulated per the National Ambient Air Quality Standards (NAAQS); globally, similar regulations are implemented on a regional basis. In oil refining, sulfur originates from the crude oil processed. Sour crudes (i.e. high sulfur crude oil) are especially troublesome and require sulfur mitigation strategies. In fluid catalytic cracking (FCC), strategies include desulfurisation of the feed via a hydrotreating unit, operations, catalyst additive technology, or a combination thereof. The former two require significant capital expense, whereas catalyst additive technology can be implemented with lower monetary investment. Catalyst additives aimed at reducing SO_x emissions interact with SO_x in the regenerator and facilitate a transformation to hydrogen sulfide (H_2S), which is released in the riser. The additive is added directly to the catalyst inventory and works immediately to combat SO_x emissions. BASF offers an additive, EnviroSOx, to meet environmental regulation requirements.

The level of SO_x emissions is dictated by the amount of sulfur in coke. All sulfur in coke is burned off in an FCC

regenerator as SO_x , thus all sulfur that ends up in coke ends up as SO_x . For non-hydrotreated feeds, 5 – 10% of feed sulfur ends up in the coke. For hydrotreated feeds, this value is higher; approximately 15 – 30% of feed sulfur ends up as coke sulfur (and ultimately SO_x) since the easy-to-remove sulfur species have been taken care of in the feed hydrotreating step. Resid feeds and feeds with high aromatic content will typically generate higher SO_x .

The mechanism of SO_x reduction involves three main active ingredients within a catalyst additive particle: cerium, magnesium and vanadium. In the regenerator, sulfur is oxidised to form SO_2 and/or SO_3 , depending on the partial pressure of oxygen. Cerium from the additive promotes the formation of SO_3 by facilitating the oxidation of SO_2 . Magnesium interacts with SO_3 to form magnesium sulfate (MgS), which is carried over to the reactor side of the FCC. In the reactor, under reducing conditions, MgS is formed, which then interacts with vanadium oxide species of the additive to form H_2S . H_2S leaves with the reactor effluent and is later separated or treated, e.g. used in the sulfur plant to produce elemental sulfur. The optimal combination of active ingredients and how they are incorporated into the final additive particle dictates the additive's efficacy in SO_x reduction ability.

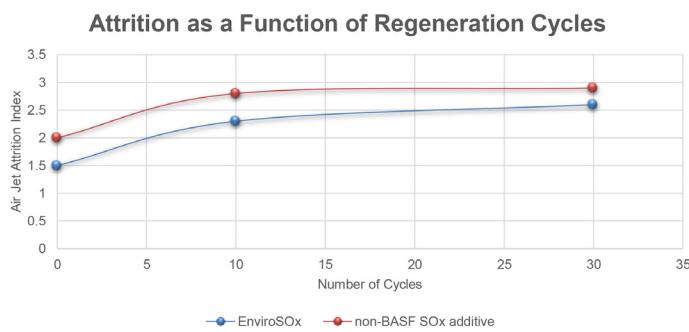


Figure 1. Attrition profile of two SO_x additives as a function of cycles.

Gulf correlation $\text{coke S} = \text{UF} (\text{slurry S})^{1.286}$

Equation 1. Gulf correlation is used to estimate uncontrolled SO_x ; UF is a unit factor, which must be uniquely determined for each unit.

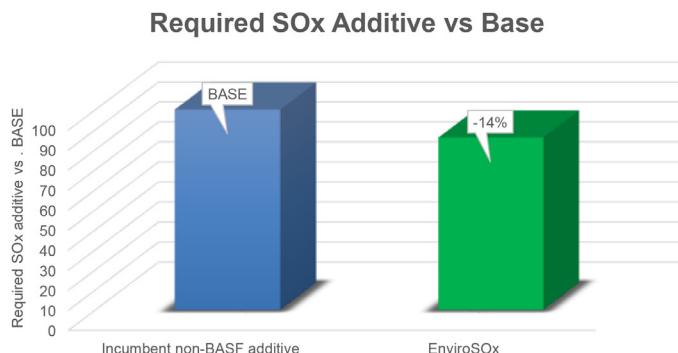


Figure 2. Statistical analysis of required additive amount, with EnviroSOx requiring 14% less to achieve the same SO_x reductions.

Attrition characteristics

An important consideration with SO_x additives is their ability to maintain structural integrity after multiple cycles in the FCC unit. Over one cycle, the particle undergoes chemical transformations, including the formation of both MgSO_4 and MgS in different steps. Both compounds have very different mass and space requirements, which puts strain on the SO_x additive particle. After many cycles, the particle is subject to degradation. Therefore, in addition to testing the initial attrition of SO_x additives, careful consideration should be placed on analysing attrition characteristics after multiple cycles. An external laboratory tested EnviroSOx and another supplier's additive, and found it gives lower attrition for the entire life cycle of the additive (Figure 1). This is especially important given some refiners' experience. In one commercial case, usage of a non-BASF SO_x additive resulted in excessive attrition of the additive, as indicated by an increase in magnesium and cerium in the fines. The fines accumulated on the expander blades as deposits, causing an imbalance and ultimately a shutdown of the critical equipment and the FCC unit.

Measuring the efficacy of SO_x reduction additives

When predicting uncontrolled (no additive use) SO_x emission, many variables influence SO_x including the type of sulfur coming in and feed metals (for instance, metals such as iron can act as a reverse SO_x additive increasing SO_x). Slurry sulfur is the preferred method for estimating the amount of uncontrolled SO_x vs using feed sulfur. The Gulf correlation (Equation 1) is one method used to estimate coke sulfur, which can be converted to expected SO_x emissions.

Multivariate statistical analysis more accurately estimates coke sulfur and SO_x emissions levels. The analysis derives a model from refinery operating data to predict uncontrolled SO_x emissions and is therefore a more accurate representation of emissions. Once built, this model can then be used to track the efficacy of a SO_x additive.

A performance indicator used to evaluate the effectiveness of the additive is the pick-up factor (PUF), which is kg of SO_x captured divided by kg of additive used. A typical PUF is between 15 and 40. While SO_x reducing additives are employed in both full and partial-burn operations, the PUF for partial burn units is approximately half that of full burn units, and can be as low as 3–4 in very deep partial burn. The PUF is also highly dependent on various operating parameters including excess O_2 in the regenerator, regenerator temperature, stripper efficacy, catalyst circulation, air distribution and mixing in the regenerator, and partial pressure of SO_2 in the regenerator.

This article explores three cases, all using SO_x reduction additives, with different methods used to track efficiency.

Case 1: multivariate statistical analysis in a multi-vendor trial

A side-by-side full burn vacuum gasoil (VGO) unit in North America that trialled BASF's additive benefited from a multivariate statistical model to analyse the effectiveness of the additive vs the incumbent non-BASF SO_x additive. EnviroSOx was added during the startup after a long-term unit shutdown. Unstable operation of the pre-feed hydrotreater meant that SO_x reducing additive requirements were variable, and were therefore modified per the FCC need. For this case, the Gulf correlation could not be used to compare pick up factors due to the unavailability of slurry samples.

To track the SO_x additive effectiveness, BASF developed and utilised a multivariate statistical analysis model using operating data while on the incumbent additive. This multivariate approach utilised the refinery's data to correlate multiple variables to the SO_x reducing additive rate, including feed sulfur, feed API, flue O_2 , riser outlet temperature, feed rate, and dilute phase temperature. The final equation was determined using stepwise regression with second order interactions of the incumbent data. The model was then projected to the EnviroSOx period, while taking into account operating changes. A comparison of the actual addition rate and modelled addition rate showed that this period required 14% less additive to achieve the same SO_x reduction target as demonstrated in Figure 2. This demonstrates a higher PUF for the additive. Finally, the availability of reliable unit data, cooperation with refinery personnel, and BASF's advanced multivariate statistical analysis tools enabled a successful post audit.

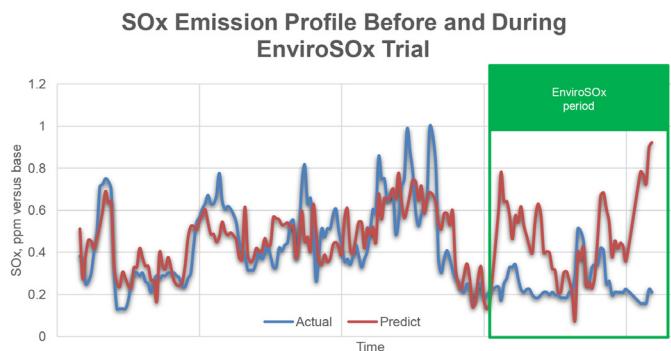


Figure 3. Refinery trial results of EnviroSOx that was pre-blended for a North American refinery, resulting in a 34% reduction in SO_x emissions; emissions were normalised to 1.

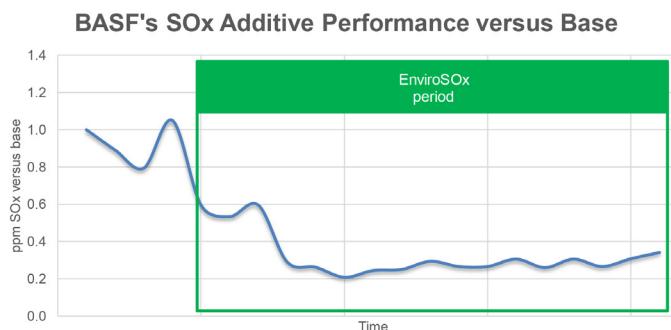


Figure 4. Refinery trial results after using BASF's SO_x additive resulting in a 72% reduction in emissions; emissions were normalised to 1 vs base.

Case 2: optimising SO_x additive use without using a loader

Common practice for environmental additives is to use a separate loader to control the addition rates. However, not all units have an extra loader since they can be cost prohibitive. Furthermore, additives that are introduced via a separate loader dilute the activity of the catalyst and can have negative effects on yield slates off the FCC.

A North American refinery trialled the BASF SO_x reduction additive that was pre-blended with the catalyst to avoid the added burden on the refinery of managing additions and utilising a separate loader. An added benefit of pre-blending additive into the fresh catalyst inventory is the ability to offset active catalyst dilution that occurs when adding via a separate loader. For this trial, a base case statistical model was built using operating data, including riser outlet temperature, oxygen injection, feed sulfur, slurry sulfur, and catalyst circulation. The base case predicted SO_x emissions accurately – it was then projected to the EnviroSOx period. The difference in predicted SO_x and actual SO_x is the result of BASF's additive.

Figure 3 shows the model predicting higher SO_x emissions than actual during the additive period – the difference is applicable to the use of the SO_x additive. Its application in this refinery resulted in a 34% reduction in SO_x emissions, allowing the refinery to operate in compliance with local regulations and alleviating other units' SO_x emission requirements within the battery limits of the refinery. These results demonstrate the

competitive advantage that the SO_x additive can offer refineries, including those who pre-blend to offset the need for an additive loader.

Case 3: monitoring SO_x additive trial in the absence of dedicated refinery equipment

One problem encountered while refineries implement SO_x additives into their emissions strategy portfolio is the availability of reliable equipment or hardware to use in conjunction with a trial. In some cases, a refinery may not be outfitted to properly take SO_x readings from effluent gas streams. However, the need for reduced SO_x emissions is still present. In a recent case such as this, BASF's technical service team, hardware solutions, and efficient SO_x additive was the three-pronged approach to solving the refinery's problem. The use of a mobile effluent gas monitoring equipment and on-site training enabled the refinery to obtain a baseline of SO_x emissions (without the additive) and allowed for the continual monitoring after adding the SO_x additive to the circulating inventory.

As shown in Figure 4, a reduction of 72% on average in SO_x emissions vs the steady base case was seen at the refinery after a transition period.

Past the trial period, the refinery continued to use the SO_x additive given these results. This trial was enabled by engaged refinery personnel, BASF's hardware solution, and the accompanying on-site training.

Conclusion

The use of SO_x reduction additives, which is becoming more common due to global regulatory compliance requirements, can be complementary to a refinery's existing hardware and operations to reduce SO_x emissions. SO_x reduction additives can also be employed during hydrotreater outages (e.g. unit trip, lack of H₂, turnaround during a catalyst change) or can be employed to take advantage of sour opportunity crudes. While FCC catalyst activity can be significantly diluted when over 10% additive is required, this dilution can be offset by pre-blending. Furthermore, the additive shows higher initial activity and overall better cycle stability and regeneration rates while maintaining good attrition characteristics in multiple refinery trials.

BASF's SO_x reduction additive helps to alleviate the need for high capital monies, requires less loading, shows competitive attrition in third-party testing, and allows refiners to operate within local regulatory requirements. As a lower attrition additive, it allows for reliable operation, offsetting cases seen in other refineries that resulted in FCC unit shutdowns due to ancillary equipment.

Advanced multivariate statistical analysis is an effective tool to accurately predict uncontrolled SO_x emissions and to analyse the performance of SO_x reduction additives. BASF's advanced technical service tools, including training of mobile gas effluent devices, are a key enabler for success for those without reliable gas effluent monitoring equipment.

In conclusion, the latest SO_x reduction additive innovation has demonstrated improved performance in multiple competitive trials and has helped refiners meet SO_x emissions requirements.