Reducing Sulfur Oxide Emissions from the FCC Unit

Introduction

Although the amount of sulfur oxide (SOx) emitted from FCC units is relatively small, it still accounts for most of the SOx released from oil refineries. The major options for reducing SOx emissions from the FCCU include flue gas scrubbing (FGS), hydrodesulfurization (HDS) and the use of a SOx-reduction additive. FGS requires a high capital investment and the operating costs are high. In addition, discarding the spent treating compounds, such as lime, caustic soda, or other compounds can also be problematic. HDS requires the highest capital investment but will also provide improved yields as well as lower SOx emissions. Therefore, the use of SOx reduction additives is often the preferred route taken by refiners, as they require very little capital investment and are extremely effective in reducing SOx emissions.

Due to new, more stringent, local environmental legislations Refinery A located in Western Europe was confronted with the challenge of reducing SOx emissions from the FCC regenerator.
by 30%. This is highlighted in Table III, which shows daily and yearly SOx bubble limits for the refinery before and after January 1, 2009.

Faced with the various options for tackling SOx reduction, the refinery chose the additive route and began using Super DESOX® additive in December 2008. The results of this trial will be discussed in this article.

**Super DESOX® Additive**

Super DESOX® additive was commercialised in 2003 and is based on a patented magnesium-alumina spinel structure, which has been successfully used by more than 70 refiners worldwide. To understand why this magnesium-alumina spinel structure works so well, it is necessary to examine the mechanism for the catalytic reduction of SOx emissions in the FCC unit. A schematic diagram of the oxidation and reduction reactions of sulfur compounds in the FCC unit is shown in Figure 8. In the regenerator, sulfur contained in the coke is oxidized to SO$_2$ and SO$_3$. Both of these sulfur oxides are absorbed on the SOx additive, where SO$_2$ is further oxidized to SO$_3$ in the presence of oxygen and an oxidation catalyst in the additive. In the regenerator the SO$_3$ reacts with magnesium oxide in the alumina spinel and is converted to magnesium sulfate. Compared to free magnesium oxide, the spinel in Super DESOX® additive is extremely effective for this sul-

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<th>Table III</th>
<th>SOx Bubble Limits for the Refinery</th>
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<tr>
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<td>Average SOx Bubble Limit</td>
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<td>Daily (mg/Nm³)</td>
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<td>Before 1st January 2009</td>
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<td>After 1st January 2009</td>
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**Figure 8**

Catalytic SOx Reduction Using Super DESOX® Additive
fate formation and a stable sulfate is formed under regenerator conditions. In the reactor the magnesium sulfate is reduced by hydrogen to form magnesium sulfide. Super DESOX® additive plays an important role here, too, because the magnesium in the alumina spinel is less basic than free magnesium oxide, thereby making the sulfate easier to reduce. In addition, vanadium on the spinel structure further decreases the stability of the magnesium sulfate, especially under reducing conditions, and in the presence of steam. The magnesium sulfide is then hydrolysed to a magnesium oxide in the stripper which then returns to the regenerator to complete the catalytic cycle. Super DESOX® additive has the highest SOx reduction activity on the market and has been widely utilized in SOx reduction applications.

Establishing a Baseline for Uncontrolled SOx Emissions

A number of operating variables have been identified as having significant effects on the performance of SOx reduction additives.1-3 Some of these include the presence of combustion promoters, the ratio of catalyst circulation rate to unit catalyst inventory, unit temperatures, availability of oxygen in the regenerator, feed sulfur content and SOx concentration.

Various scientific studies have shown that the fraction of thiophenic sulfur in the feed has a direct impact on the coke sulfur content deposited on spent catalyst and thus, on SOx emissions. Therefore changes in uncontrolled SOx emissions can be accurately estimated by measuring thiophenes in feed. However, it is uncommon for refiners to be able to measure thiophenic feed content on a regular basis. It is therefore recommended to estimate uncontrolled SOx emissions by measuring feed sulfur or even better with slurry sulfur (the slurry being the most aromatic product of the FCCU).

Due to the various operating variables that can affect SOx additive performance, it is necessary to establish a baseline of uncontrolled SOx emissions to be able to calculate the true SOx reduction caused by the additive. This baseline is calculated by performing correlations for every relevant parameter based on pre-trial unit data. To establish a baseline for Refinery A, approximately three months of unit data was used.

We observed that in general parameters such as slurry density and slurry sulfur content correlated well with SOx emissions. However, due to a lack of slurry measurements, it was decided to use feed properties instead. In this respect, the main parameters turned out to be feed sulfur content (S.charge), vacuum residue throughput (RSV) and flue gas oxygen content, as shown in Figure 9. Using the excellent data from the refinery, the correlation in Figure 10 was established using the normalized SO2 values from the pre-trial period (from October 21, 2008 to January 12, 2009). The high value of R2 (86.9) signifies the extremely good correlation obtained.

As expected, it can be seen that increased feed sulfur plays a major role in the above correlation, i.e. SOx emissions increase with increasing feed sulfur. In addition, increased residue
throughput can also be expected to increase SOx emissions, which is indeed observed in the correlation. The incorporation of more residue results in increased SOx emissions due to the more refractive nature of its sulfur-containing compounds that will thus end up more readily in the coke on catalyst. The other important variable in the correlation is flue gas oxygen content. Increasing oxygen promotes the oxidation of coke on spent catalyst and thus the oxidation of sulfur species to SOx.

**Trial of Super DESOX® Additive at Refinery A**

The Super DESOX® additive performance at Refinery A is estimated by comparing the measured SOx emissions with the predicted uncontrolled SOx emissions, of which the latter is based on the correlation in Figure 10. To reach the target of reducing SOx emissions by 30% Grace Davison recommended using Super DESOX® additive at 0.8 wt.%, with a prior period of base loading to accelerate the introduction of the additive in the inventory. However the refinery decided not to have a base-loading period and began using 0.8 wt.% of Super DESOX® additive directly. The additive pre-blended with fresh catalyst was delivered to Refinery A on January 12, 2009 and entered the unit around January 19th as seen from the subsequent and obvious drop in flue gas SOx emissions, shown in Figure 11.

* Flue gas SOx was measured as SO2 by an online analyser, and the SO2 values are normalized to 3% excess oxygen in flue gas.

![Figure 11](image-url)
The effect of Super DESOX® additive was immediate with average SOx reductions of 23% observed within the period of January 19th to February 15th in which the additive was pre-blended at 0.8 wt.%. This can be effectively considered as a base-loading period during which a stationary concentration of additive is reached in the inventory. It was subsequently decided to reduce Super DESOX® additive pre-blending levels to 0.5 wt.% during February 16th to March 29th. The average SOx reduction performance during this period remained high at 25%. In the subsequent period between March 30th and June 30th, this refinery decided to increase Super DESOX® additive pre-blending levels to 1.5 wt.% to gain an idea of just how much SOx reduction could be achieved, and during this period the average reduction rate increased to 41%. Starting on September 28th, the refinery started pre-blending Super DESOX® additive at 1.8 wt.% due to increased feed and slurry sulfur levels, resulting in average SOx-reduction levels of 66%.

Figure 11 shows that SOx values measured over time were somewhat volatile. This is due to the variations in feed and slurry sulfur content during the trial period, which is reflected in the predicted uncontrolled SOx levels. As shown in Figure 12, feed sulfur varied between 0.31 and 0.52 wt.%, while slurry sulfur varied between 0.6 and 0.9 wt.%.

In terms of retention levels of Super DESOX® additive the refinery acknowledged excellent performance. Indeed, Super DESOX® additive is recognized in the market for its retention properties.
During the period where Super DESOX® additive was added at 1.5 wt.% a serious inventory deactivation occurred due to increasing vanadium contamination of the Ecat, as shown in Figure 13. It is testament to the superior performance of Super DESOX® additive that even with the dramatically increased Ecat vanadium levels, and the subsequent drop in MAT activity, levels of SOx reduction were still achieved.

Conclusions

As a consequence of increasingly stringent local environmental regulations, Refinery A was forced to reduce SOx emissions by 30%, and Grace Davison recommended the use of Super DESOX® additive as the quickest and most cost-effective route to achieve this. Using the excellent data from the refinery a baseline for uncontrolled SOx emissions was established so that an accurate evaluation of the SOx-reducing performance of Super DESOX® additive could be evaluated. The trial of Super DESOX® additive was considered a complete success achieving the refineries objectives even with lower amounts of the additive than first predicted. Refinery A is now using Super DESOX® additive continuously as a simple, efficient and cost-effective solution to reduce flue gas SOx emissions.

References