



Controlling FCC SO_x emissions with SO_x reduction additive technology

A novel additive with optimized metal dispersion and metal-support interaction achieved significantly lower daily operating cost of SO_x removal from an FCC unit – a refinery case study.

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Government agencies continue to introduce stricter legislation to reduce the amount of sulphur oxide emissions. Sulphur oxides (SO_x) are pollutants that contribute to the formation of acid rain, as well as particulate pollution.¹ Sulphur present in feedstock is the main source of SO_x emissions from oil refineries, and the fluid catalytic cracking (FCC) unit is responsible for up to 90% of oil refinery SO_x emissions.² Typically, 2-10% of FCC feed sulphur ends up as sulphur contained in the coke on spent catalyst.² When the spent catalyst is regenerated, the sulphur is oxidised to SO₂, SO₃, and so on. Left untreated, SO_x emissions are emitted into the environment.

FCC SO_x emission reduction solutions

Process technologies and high-performance catalysts have been developed to reduce FCC SO_x emissions.^{2,3,4,5} The main solutions used are:

1. Feed selection and/or pretreatment to reduce FCC feed sulphur.
2. Hardware solutions which remove SO_x from the FCC flue gas (such as flue gas wet gas scrubbers).
3. Innovative SO_x reduction additives.

Hardware solutions often require considerable capital investment. On the contrary, SO_x reduction additives only require a small capital investment, such as the addition of an additive addition system (AAS).⁶ Furthermore, SO_x reduction additives are suitable for a wide range of operating conditions. Thus, SO_x reduction additives are the preferred solution for many FCC units. Whichever solution is used, a key benefit often overlooked is the opportunity to use the SO_x reduction technology to process high-sulphur, low-cost feeds, which unlocks the potential to increase FCC margin.

FCC SO_x reduction additive chemistry

SO_x reduction additives are injected into the FCC regenerator, where they mix with the circulating catalyst. SO_x is captured by the additive in the regenerator, and the circulating catalyst transfers the captured SO_x to the reactor. This captured SO_x is converted to hydrogen sulphide (H₂S) in the reactor. H₂S is removed from the FCC fuel gas and LPG product in the unsaturated gas plant. H₂S is eventually converted to elemental sulphur, which the oil refinery can sell.

Typical SO_x reduction additive levels in the catalyst inventory range from 1 to 10%, although some FCC units are being required to use additives at the 20% level.² In FCC units with full-burn regenerators, SO_x reduction additives can achieve and maintain SO_x reduction levels of >95%.² In partial-burn regenerators, the achievable SO_x reduction depends on the availability of SO₃ in the regenerator.²

As the SO_x additive injection rate increases, suppliers should provide detailed guidelines to enable small adjustments to be made in the FCC and unsaturated gas plants, the sulphur recovery system, the product handling area, and procurement systems. Therefore, a global supplier with additive production, laboratory support, quality control, FCC, oil refinery, and supply chain experience is highly desirable. The SO_x removal process has multiple steps.

Step 1: Oxidation

Under typical regenerator operating conditions, the ratio of SO₂ to SO₃ is about 9 to 1 or greater. An oxidation package is needed to convert SO₂ to SO₃ because the SO_x reduction additive is more effective at capturing SO₃ than SO₂. Reaction 1 shows the overall reaction.



Step 2: Sorption

SO₃ is captured by the SO_x reduction additive. The SO₃ is chemisorbed onto the additive as a metal sulphate (where M represents the metal site). Once the additive has picked up the SO₃ and adsorbed it as MSO₄, it circulates along with the catalyst to the reactor. Reaction 2 shows the overall reaction.



Step 3: Release

In the reducing environment in the reactor, the additive releases sulphur as H₂S. Reaction 3 shows the overall reaction.



The active metal oxide site of the additive is regenerated and capable of repeating the sorption-desorption cycle many times.

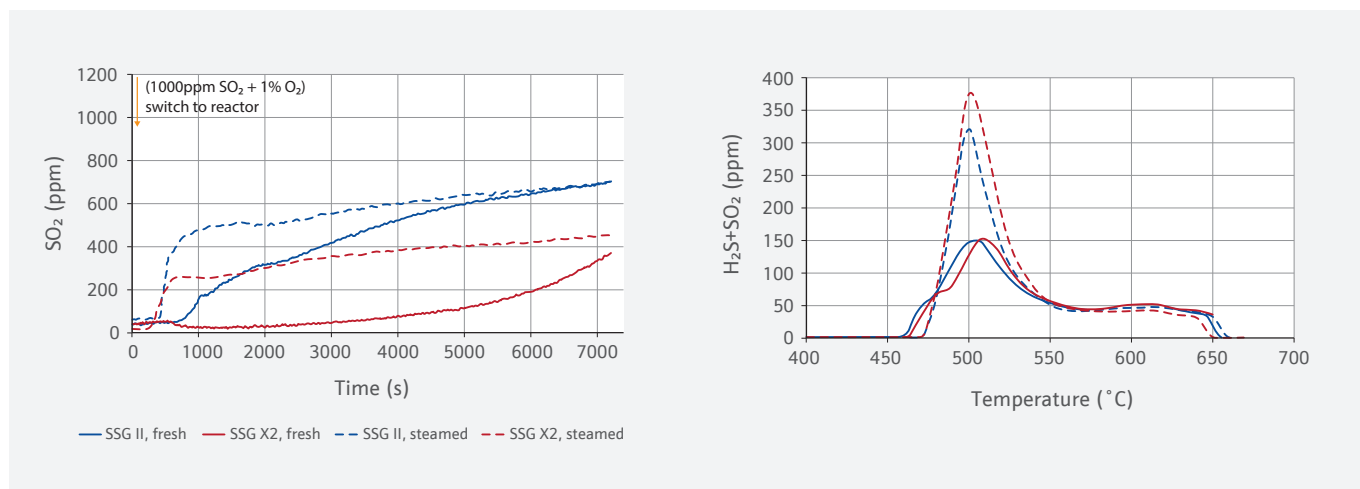


Figure 1 SOx breakthrough (left) and SOx release (right) profiles

Development of a novel SOx reduction additive

Johnson Matthey's work around SOx reduction additive performance highlighted the significant contribution of Step 1: Oxidation. Cerium oxide plays a crucial role in the selective oxidation of SO₂ to SO₃.⁷ Research revealed that a high number of active sites, active site reducibility, and active site stability improve additive performance. The development of an optimised metal dispersion and metal-support interaction led to a significant increase in the number of active sites for oxidation compared to the current benchmark additive **SUPER SOXGETTER™ II (SSG II)**.

Besides enhancing the efficiency of SO₂ to SO₃ oxidation, an optimised cerium dispersion and metal-support interaction also provided better particle sintering resistance, thereby improving the stability and activity of the additive over time. It is understood that cerium oxide particle sintering leads to rapid deactivation of SOx reduction additives due to a reduction in the number of active sites available for Step 1: Oxidation.⁵

The new SOx reduction additive, **SUPER SOXGETTER X2 (SSG X2)**, allows FCC unit operators across the globe to:

1. Achieve the same SOx reduction using less additive; in other words, reduce their daily operating cost.
2. Expand their FCC unit operating window; in other words, improve their FCC unit margin.

Laboratory physical properties analysis

The new additive's metal interaction with the support has been optimised without compromising its excellent physical properties, as exemplified in Table 1. These SOx reduction additives exhibit low attrition and fines and possess a suitable particle size distribution, apparent bulk density (ABD), and surface area (SA), making them ideal for FCC applications.

Physicals	SUPER SOXGETTER II	SUPER SOXGETTER X2
SA, m ² /g	113	113
A.I., w/w	1.1	1.3
ABD, g/cm ³	0.85	0.85
APS, μm	92	95

Table 1: Physical properties of **SSG X2** vs **SSG II**

Sorption-desorption laboratory testing results

Figure 1 presents a comparison of the SOx uptake and release capabilities of **SSG X2** and **SSG II** using two distinct benchtop-scale setups for evaluating SOx removal additives. Quartz reactors in a fixed fluid bed configuration were used to evaluate one-pass SOx uptake and release abilities. SOx pick-up was carried out by flowing a 1,000 ppm SO₂/1%O₂/N₂ gas mixture over a sample after it had been heated in N₂ at 700°C for 30 minutes. The effluent gas was monitored by an IR analyser. Temperature-programmed sulphur release (TPSR) with reducing gas (such as 5% H₂/N₂) was used

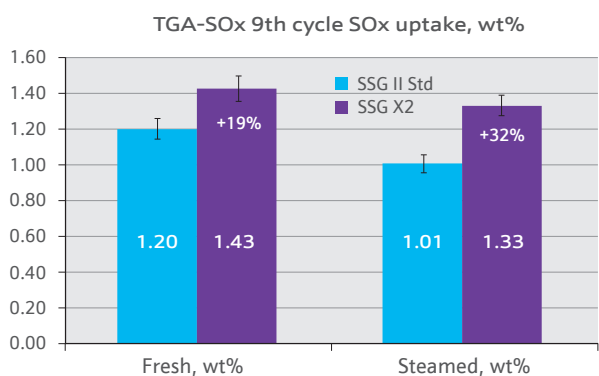
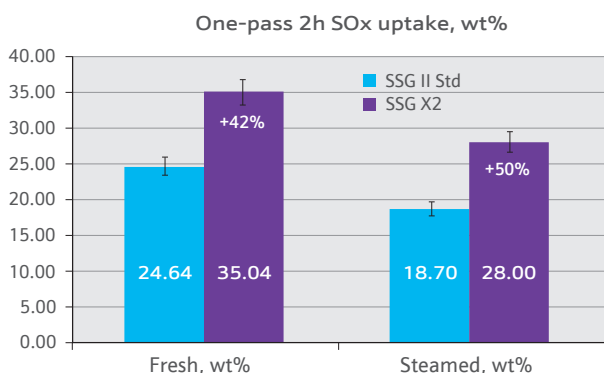


Figure 2 Laboratory performance ranking of **SSG X2** and **SSG II**

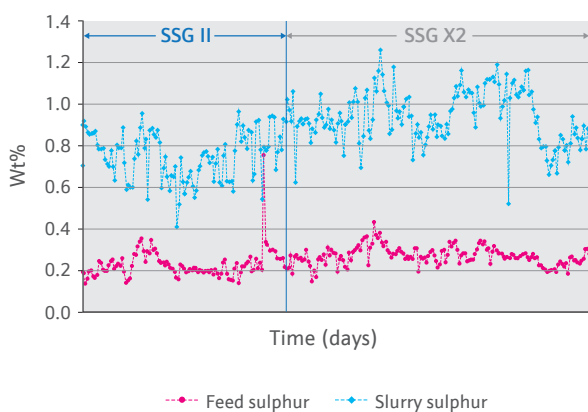


Figure 3 FCC feed and slurry sulphur

to study the sulphur release of a sulphated sample. The effluent gas was sampled at desired time intervals and analysed by a flame photometric detector (FPD).

These results indicate **SSG X2** exhibits higher SOx uptake ability in activity evaluation. In breakthrough or one-pass SOx pick-up testing, the fresh and steamed **SSG X2** demonstrated a 42% and 50% increase in SOx uptake ability, respectively, compared to **SSG II**. Additionally, a thermogravimetric analyser (TGA) coupled with a mass spectrometer (MS) was employed to conduct multi-cycle SOx pick-up and release testing. Results revealed a 19% and 32% enhancement in SOx uptake for **SSG X2** compared to **SSG II** (see Figure 2).

Regarding sulphur release, both additives displayed similar onset temperatures and release profiles (Figure 1). These laboratory findings suggest **SSG X2** exhibits superior SOx reduction capabilities compared to **SSG II**.

Refinery commercial trial

Overview

In this case study, **SSG X2** was used at a US Gulf Coast refinery. The typical feed sulphur is 0.26 wt%, and the typical slurry sulphur is 0.84 wt%. The refinery uses a dedicated Additive Addition System (AAS) to optimise the daily addition rate of SOx reduction additive to control the FCC flue gas SOx emissions. The trial compared the performance of **SSG X2** and **SSG II**. The trial was closely monitored by the refinery and Johnson Matthey team.

Comparison summary	SSG II	SSG X2	Delta	Delta%
Additive addition rate, lb/day	333	295	-38	-11%
Additive concentration, wt%	3.30	3.05	-0.25	-8%
Feed sulphur, wt%	0.22	0.27	0.05	24%
Slurry sulphur, wt%	0.73	0.94	0.21	30%
Ecat Fe, wt%	0.39	0.43	0	10%
Flue gas O ₂ , vol%	0.81	0.83	0	2%
Regenerator temp, F	1,334	1,340	6	0%
Riser outlet temp, F	1,005	1,012	7	1%
Uncontrolled SOx, ppm	235	329	94	40%
Controlled SOx, ppm	21	22	1	3%
SOx reduction, %	91	93	3	3%
Pick-up factor (PUF), lb/lb	18	26	8	44%

Table 2: Key trial conditions and results

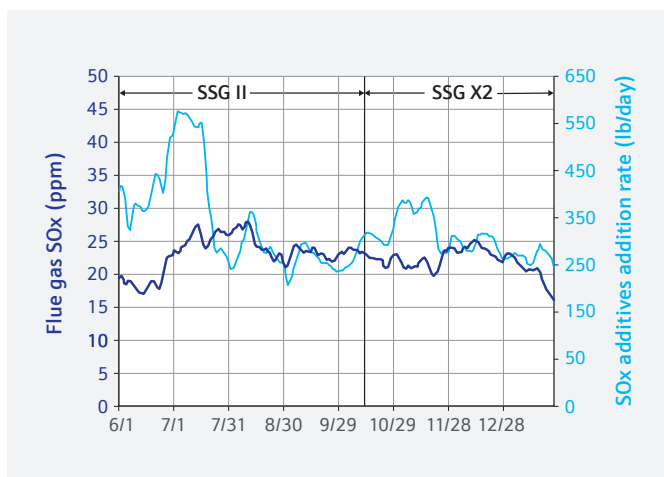


Figure 4. FCC flue gas SO_x emissions and SO_x reduction additive injection rate

A comparison of plant data for the different operating periods was completed. In addition, a comparison of Ecat samples for the different operating periods was completed. The trial operating periods were:

1. Base line: **SSG II**
2. New additive: **SSG X2***
3. Back to baseline: **SSG II**.

*The SSG X2 trial period was five months.

Trial results

FCC feed sulphur varied between 0.22 and 0.27 wt%, and the slurry sulphur varied between 0.73 and 0.94 wt% (see Figure 3). At similar operating conditions, **SSG X2** controlled the FCC flue gas SO_x emissions using 11% less additive (see Figure 4), compared to **SSG II**.

Table 2 summarises the key trial conditions and results. At the same slurry sulphur level, **SSG X2** demonstrated the potential to control FCC flue gas SO_x emissions using up to 25% less additive (see Figure 5), compared to **SSG II**. SO_x pick-up factor (PUF) quantifies the efficiency of SO_x removal. It is defined as the amount of SO_x removed per day per pound of SO_x reduction additive added per day. SO_x PUF is different for each FCC unit and depends on several variables. At this refinery, the typical PUF was 18 using **SSG II**. For a wide range of operating conditions, the PUF for **SSG X2** was greater (Figure 6).

To complement the FCC trial results, an Ecat evaluation was performed. Multi-cycle TGA-MS-SO_x experiments were conducted. Figure 7 illustrates the results obtained under identical testing conditions, revealing a noticeable pattern of enhanced SO_x pick-up ability in Ecats

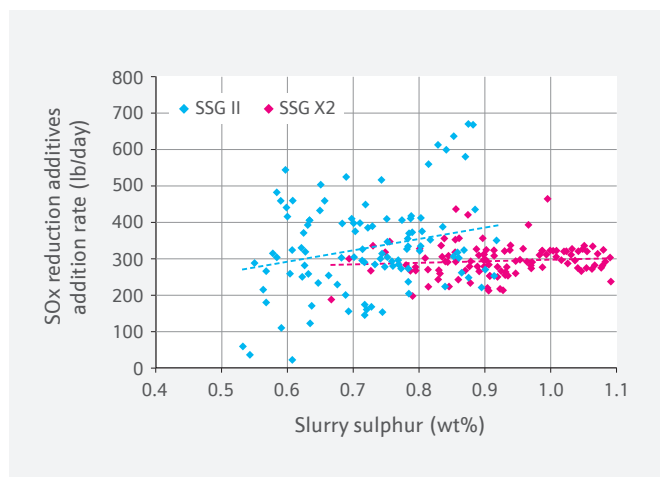


Figure 5. SO_x reduction additives addition rate vs slurry sulphur

containing higher concentrations of **SSG X2**. A steady state was achieved after eight weeks, exhibiting an approximate 36% improvement. Following the return to the baseline, the SO_x uptake abilities of the Ecats began to decline and returned to their pre-trial levels within approximately eight weeks.

Trial conclusions

In this trial, **SSG X2** enabled this US Gulf Coast refinery to use 20% less additive while achieving the same SO_x reduction for a wide range of typical operating conditions. An additional benefit was less additive handling, saving operators' time. There was also a small reduction in catalyst disposal.

Conclusions

Cost-effectively managing SO_x emissions is a challenge for many FCC units. Johnson Matthey has developed and successfully commercialised a novel SO_x reduction additive, **SUPER SOXGETTER X2**, which incorporates improved metal dispersion technology. Higher SO_x capture with this additive allows FCC unit operators across the globe to:

1. Achieve the same SO_x reduction using less additive; in other words, reduce their daily operating cost.
2. Expand their FCC unit operating window; in other words, improve their FCC unit margin.

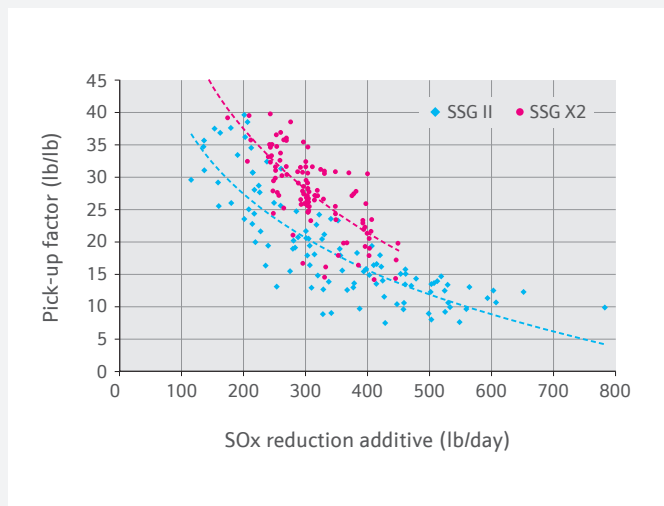


Figure 6. Pick-up factor vs SOx reduction additive addition rate

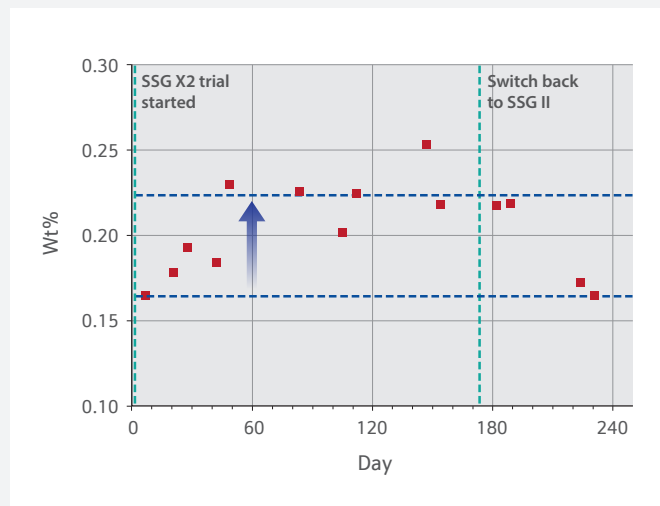


Figure 7. Laboratory SOx reduction additive performance ranking

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