FCC SOx additives and security of supply

Rare earth prices could accelerate again as a result of trade tensions

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Although it happened nearly a decade ago, refiners and suppliers still bear scars from the last spike in rare earth prices that occurred in 2010-2012 and the severe impact this had on refinery bottom lines. Export restrictions on rare earth raw materials imposed by China, which accounts for 94% of global production, caused a 30-fold increase in market price of some of these commodities.[1] This hurt the refining industry in two areas due to a reliance on particular rare earths: lanthanum oxide, which is a key component of FCC fresh catalyst,[2] and cerium oxide, which is a crucial component of FCC SOx reduction additives.[3]

The use of a catalyst additive is a known straightforward and flexible way to meet FCC SOx emission limits and has become accepted technology for many refiners. Alternatives for rare earth components in FCC catalyst and SOx additive formulations were studied, and although thrifting and optimisation helped minimise short-term pain, effective alternatives were not successfully implemented before the rare earth bubble burst in 2012.[9] Therefore the refining industry remains in a precarious position and at the mercy of future price spikes, with China remaining the major producer of rare earths.[4] Reports suggest a likelihood that, in the case of faltering trade talks with the US, China could implement new trade sanctions on rare earth minerals.[4] A harbinger of this possibility was seen in May 2019 when prices of rare earth materials spiked almost 50% merely on rumours of another embargo.[5] It is expected that future sanctions would apply to raw materials rather than finished goods containing rare earth, thus only impacting importers of rare earth components and raw materials, not those exporting final catalysts or additives.

Here, our focus is on cerium oxide as a component of FCC SOx reduction additives, and how alternative additive supply options offer a solution to manage risk. Utilising a broad approach to sourcing SOx reduction additives, Unicat and G. W. Aru, LLC offer security of supply and high performance.

SOx reduction chemistry

SOx reduction additives typically comprise of three key components, each having a different function within the FCC operation. The largest proportion of a SOx additive by mass is magnesia-alumina mixed metal oxide sorbent, which is effective for absorbing sulphur trioxide (SO_3) in the regenerator as magnesium sulphate. The magnesia to alumina ratio determines whether the additive is referred to as a spinel or hydrotalcite-type with low or high magnesia content respectively. SOx is a combination of SO_3 and SO_2 where these species exist in equilibrium, which favours SO_2 in the approximate proportions 95% SO_2 to 5% SO_3.[6] Since the sorbent can only absorb SO_3, the efficiency of SOx removal would be severely limited if SO_2:SO_3 equilibrium was not quickly restored local to the SOx additive absorption site.[6] Cerium oxide is included in the additive formulation to assist oxidation of SO_2 to SO_3 and improve effectiveness. It has been found that SOx additives lacking cerium oxide result in low overall SOx absorption, measured commercially as low pick-up efficiency.[7] The final step is SOx additive regeneration in the FCC riser/reactor. Here, a non-mobile vanadium component is used to promote reduction of absorbed sulphate to hydrogen sulphide. H_2S is removed from the process in the FCC dry gas stream. Once the H_2S is released, magnesium sulphate returns to magnesium oxide and is available for further SOx pick-up in the regenerator.[6] This circular process continues until activity is lost through sintering of cerium oxide and densification of the magnesia-alumina phase.

The most effective way to determine which SOx additive is best for your FCC operation is by performing a series of industrial trials

Although use of rare earths has been a sensitive issue for refiners due to past experiences of price spikes, high performance SOx additives need to correctly balance each component of the tri-functional system to function efficiently. FCC unit configuration and operation will dictate the relative importance of each component where formulations may be optimised for full burn, partial burn, or low reactor temperature operation. For example, in typical full burn units the limiting factor for SOx pick-up is believed to be absorption site availability. Conversely, in partial burn operations oxidation of reduced sulphur species to SO_3 is critical. For low riser temperature operation, otherwise called diesel or distillate

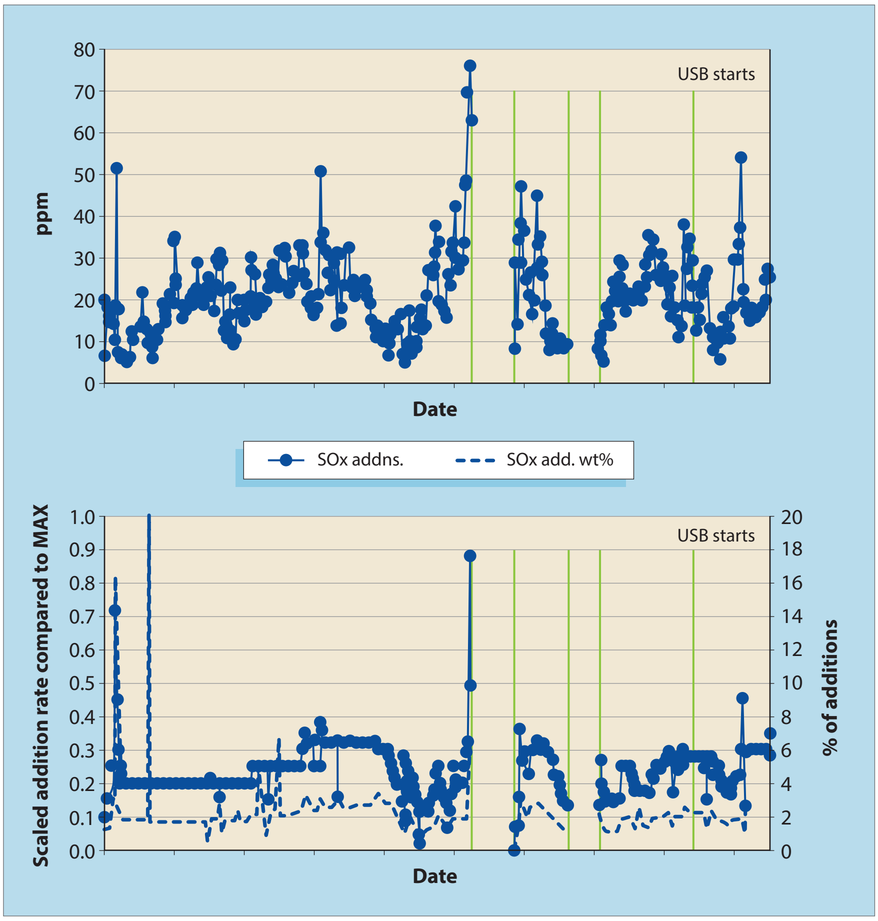

Figure 1 (a) Time plot of Refinery A flue gas SOx emissions **(b)** Time plot of Refinery A SOx additive additions. Vertical lines indicate shutdowns and the start of USB-M60 trial

mode, good SOx additive regeneration is essential for release of sulphate, which is less favourable at lower temperatures. Many refiners find that they switch between such modes frequently. In these cases, it is best practice to select the optimum SOx additive for the current operational strategy as it is also found that some SOx additive types are incompatible with certain modes of operation. In all cases, a SOx additive with the appropriate magnesium to aluminium ratio and with good dispersion within the particle should be selected. In summary, a superior SOx reduction additive should excel in all three of these areas, and refiners should work with a competent additive supplier to ensure the correct SOx additive is chosen for their operation.

SOx reduction additive trial

The most effective way to determine which SOx additive is best for your FCC operation is by performing a series of industrial trials. Daily pick-up factor (PUF), as defined in the following equation, is a calculation typically used to quantify SOx additive effectiveness:

Daily PUF = (mass of SOx removed per day) / (mass of SOx additive added per day)

Daily PUF may initially be estimated through simulation models or from experience of similar FCC unit responses. However, an accurate daily PUF should be validated by industrial test as local fluctuations in the regenerator (such as spent catalyst mixing or maldistribution) or riser (regeneration efficiency) operation can greatly affect true SOx additive response in any FCC unit. Daily PUF from an industrial test for one FCC unit cannot be assumed to be a direct facsimile of daily PUF expected for another FCC unit, no matter how similar the operation. The same can be said regarding SOx additive performance straddling a major turnaround, particularly if known mechanical issues were repaired or design enhancements were introduced during the turnaround. This is also true for emergent operational issues following unit shutdown or start-up compared to stable operation. In all cases, it is appropriate to re-evaluate SOx additive performance to ensure the best performing additive is selected for the operation.

Ultra SOxBuster additives

Ultra SOxBuster (USB) additives are offered by G. W. Aru, LLC to refiners in North America, and under the Unicat brand in Europe and around the world. These additives are produced by manufacturing partners in China and other locations worldwide. Chinese manufacturers have been producing high quality additives for domestic markets for many years. SOx additives conforming to standards of western catalyst and additive manufacturers, for example in the US and Europe, have been developed in China for use in Chinese refineries. The quality of these additives is consistent with those produced in western markets but cost structure differs significantly. Access to these FCC additives is now made available to refiners outside of China with local technical support close to the end user. Moreover, the sourcing approach taken by G. W. Aru, LLC and Unicat means refiners are offered a wide selection of SOx additive types to ensure the best SOx additive is selected for the operation. Included in the Ultra SOxBuster range are USB-M30 and USB-M60, which contain approximately 35 wt% and 60 wt% MgO respectively. These additives have similar physical properties and ceria and vanadium content as SOx additives currently used by refiners today.

Trial at a US refinery (Refinery A)

Ultra SOxBuster-M60 was evaluated at Refinery A, which is a site in the US belonging to a major international oil refining company. Results were compared against a top selling competitive SOx additive that had been in use at this site for many years on a continuous basis. As both additives are hydrotalcite based with similar physical properties, performance on a per mass basis was expected to be similar. Like-for-like performance would give the refiner access to an alternative, lower cost SOx reduction additive to achieve their compliance requirements. Proving the performance of USB-M60 also gives this refiner confidence that SOx control costs would be manageable should cerium oxide prices again escalate following trade disputes. Unicat and G. W. Aru, LLC uses their knowledge of FCC operations and experience of SOx additive performance to analyse the trial results and determined that USB-M60's performance exceeded that of the competitive SOx additive.

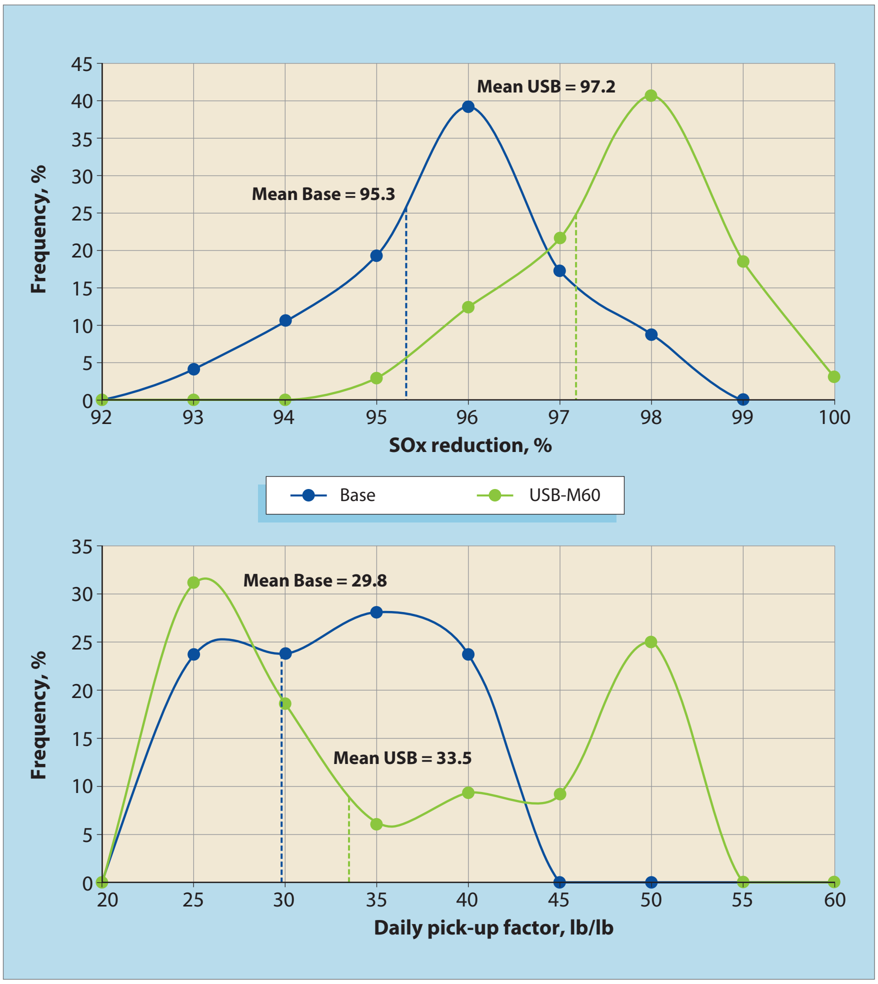

Figure 2 (a) Histogram of Refinery A SOx reduction **(b)** Histogram of Refinery A daily pick-up factor

Upon commencing the trial, the first indication of a positive response with USB-M60 was that flue gas SOx emissions were maintained at the required low level (see **Figure 1a**). Additive consumption is also maintained within normal range to achieve this low SOx emissions level (see **Figure 1b**). Although these first views are positive, deeper analysis is required. This starts with comprehensive unit monitoring analysis using time plots to ensure absence of, or to account for, fundamental changes in FCC feed properties, operation, or catalyst properties throughout the trial period that may corrupt test data or challenge trial validity. Once representative test periods are identified, average results are compared to determine superficial quantitative differences between test periods (see **Table 1**).

> **An industry recognised technique to differentiate performance in FCC operations is cross-plotting**

Although average data offers a convenient overview of trial results, it gives little information on repeatability, consistency, presence of outliers, or the ability to achieve certain target results (such as frequency and reliability of exceeding 95% SOx reduction or number of days under 20 ppm SOx emissions, for example). Histograms are used to further contextualise the results observed (see **Figure 2**). Using these methods of analysis confirms that the performance of USB-M60 exceeded that of the previous additive.

However, viewing bulk average data does not account for unit shifts and fluctuations which are unavoidable in the majority of FCC operations. Also not accounted for are certain dynamic variations and sensitivities that are important in SOx additive trials, such as changes in SOx additive addition rate or addition strategy. An industry recognised technique to

Refinery A mean average FCC data during SOx additive trials

Period	Baseline	USB trial
Feed S, wt%	0.21	0.22
Feed CCR, wt%	0.94	1.14
Rgn. dense T, °F	1324	1320
Cat. circ., tpm	Base	Base x 0.98
Air:coke, wt/wt	=	=
Excess O_2, vol%	2.0	2.3
Slurry S: Feed S, wt/wt	2.9	3.0
Slurry S, wt%	0.6	0.7
SOx additive addns., lb/day	Base	Base x 1.09
SOx reduction, %	95	97
Daily pick-up factor, lb/lb	30	34
SOx emissions, ppm	24	19

Table 1

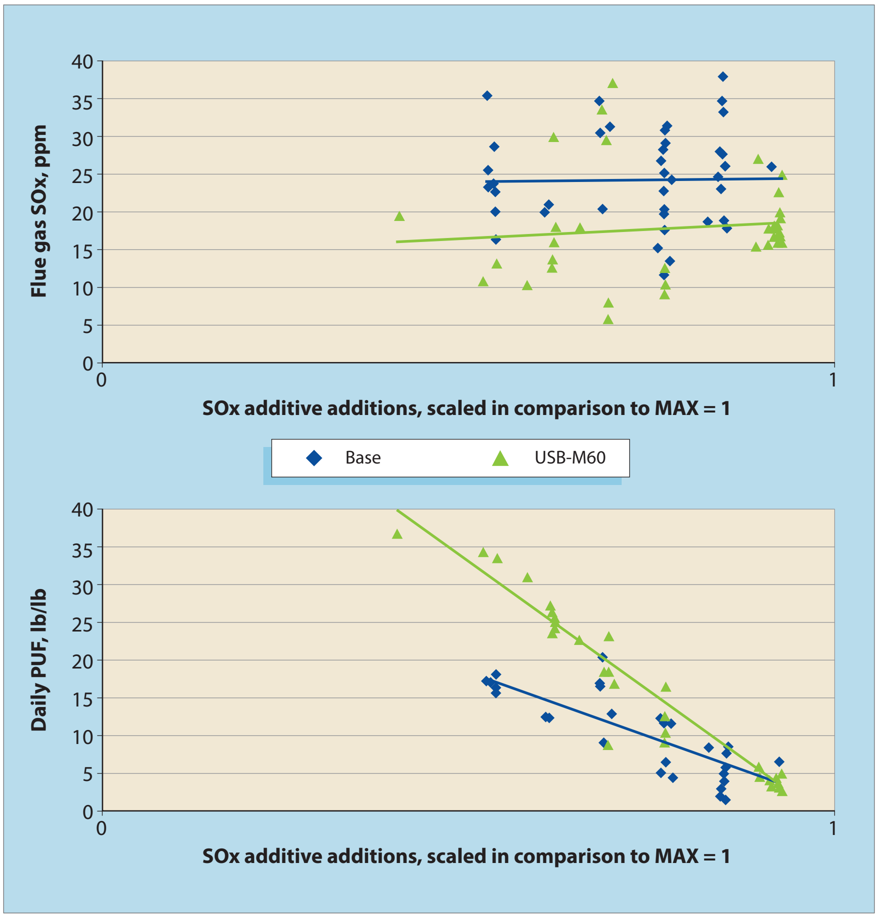

Figure 3 (a) Refinery A SOx emissions plotted as a function of SOx additive additions, and **(b)** Refinery A daily PUF plotted as a function of SOx additive additions

differentiate performance in FCC operations is cross-plotting. This method is used to observe changes in key dependent variables at a fixed single independent variable. Cross-plots show that at constant SOx additive addition, SOx emissions are 25% lower with USB-M60 than with the previous additive (see **Figure 3a**). As expected, daily PUF for USB-M60 is higher compared to the competitive additive (see **Figure 3b**). This is taken as the clearest conclusion of relative additive performance: USB-M60 is 20-25% more efficient than the previously used additive.

Following complete, multi-faceted, and precise analysis by FCC technical service engineers, conclusions can be drawn that USB-M60 outperformed the previous SOx reduction additive at Refinery A (see **Table 1**). This increased performance directly translates into cost savings for the refiner as well as an ability to improve FCC SOx control through use of a more active and therefore more responsive additive.

Conclusion

Introduction of Ultra SOxBuster additives offers refiners the opportunity to increase cost savings and future-proof themselves against potential rare earth price spikes. Industrial trials have been conducted that prove superior performance versus incumbent SOx reduction additives. Results from one such trial have been discussed here.

UNICAT and G. W. Aru, LLC help refiners to reduce environmental control costs through use of FCC additives and support from an experienced team. G. W. Aru LLC, Unicat Catalyst Technologies, Inc. and Magma Catalysts are partners to bring cost-effective and innovative catalyst solutions including the Magma steam methane reforming catalyst to refiners worldwide. This alliance utilises Unicat's existing support infrastructure and management of regulatory requirements such as REACH in the European Union. This collaboration has brought multiple benefits and gives refiners access to new technology.

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