

Passivating vanadium in FCC operations

Three in-unit trials demonstrated ability to control various oxidation states of vanadium with strong passivation technology

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Sixty per cent of fluid catalytic cracking (FCC) units are faced with the challenge of processing feedstocks containing at least some resid as a fraction of the feed. Vanadium passivation and resid catalyst technology are critical to minimising the negative impacts of vanadium in these resid feeds since, compared to processing vacuum gas oil (VGO), resid feeds pose an additional challenge of dealing with the harmful effects of contaminants.

Vanadium enters the FCC unit in porphyrin complexes present in the feed and then deposits on FCC catalyst as feed is cracked. As catalyst circulates through the FCC, the inventory moves between the riser, a reducing environment, and the regenerator, an oxidising environment containing steam and SO_x. This means that, at any given time, vanadium in the FCC exists in a variety of oxidation states, giving rise to vanadium's notorious and detrimental mobility within the catalyst circulating inventory.

The most pronounced impact of vanadium is illustrated in **Figure 1**. This figure shows BASF benchmarking data of FCC equilibrium catalyst (Ecat) activity vs the vanadium and sodium level on Ecat collected from FCC units across the world. While there is a large amount of scatter due to the number of variables impacting Ecat activity, these data help visualise a trend well understood in the FCC industry: higher vanadium and sodium result in lower catalyst activity (all else being equal).

Numerous studies by various researchers around the world describe the destructive impact of vanadium in FCC, as illustrated in Figure 1. One study demonstrated that the mechanism for the destruction of Y-zeolite in FCC catalyst is the result of a reaction involving vanadic acids, sodium, and steam. Thus, the relationship between activity and the vanadium and sodium level seen in Figure 1 is expected.

Vanadium presents an additional challenge as a dehydrogenation catalyst when in the oxidised form. While this dehydrogenation impact is not as pronounced as with nickel, it can still lead to increased hydrogen and delta coke, potentially introducing unit limitations due to wet gas constraints, elevated regenerator temperatures, and decreased production of valuable liquid products.

While one solution to maintaining Ecat activity with higher vanadium levels is to increase fresh catalyst additions, this may not always be ideal. Increased catalyst additions result

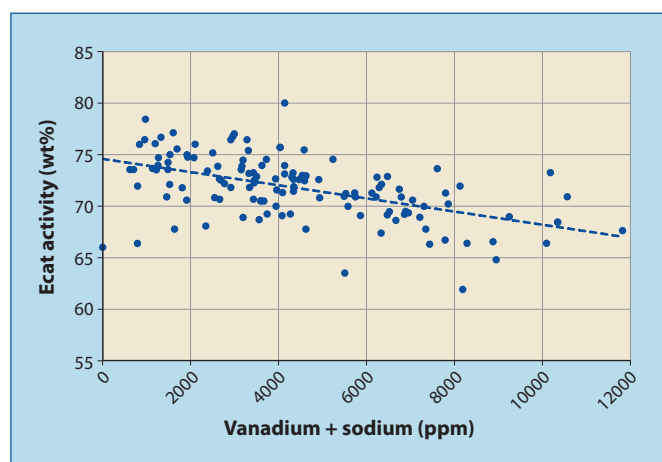


Figure 1 Benchmarking data of Ecat activity vs vanadium and sodium

in increased operating cost for FCCs; furthermore, catalyst additions are ultimately limited by the capabilities of an FCC unit's fresh catalyst loader.

Fortunately, there are several catalyst design options to counteract the negative impacts of vanadium and help mitigate extra fresh catalyst additions needed to maintain activity in the face of elevated vanadium levels. To a point, the zeolite amount or rare earth to zeolite of the FCC catalyst can be increased to improve activity maintenance of the catalyst. Additionally, nickel (Ni) passivation could be used to reduce delta coke resulting from any nickel contaminant present. However, there are limitations to each of these techniques, and vanadium passivation technologies have proven to be a preferred way to deal with moderate to high levels of vanadium.

Vanadium passivation and sulphur tolerance

Vanadium passivators, often referred to as vanadium 'traps', react with vanadium in the FCC to immobilise and passivate the metal. This prevents vanadium from participating in reactions that generate hydrogen and coke or destroy zeolite and catalyst activity. Early versions of vanadium traps used alkaline earths, such as CaO or MgO, as active sites to react with vanadium. However, a competing reaction exists, which can hinder vanadium passivation.

SO_x present in the FCC regenerator can react with alkaline

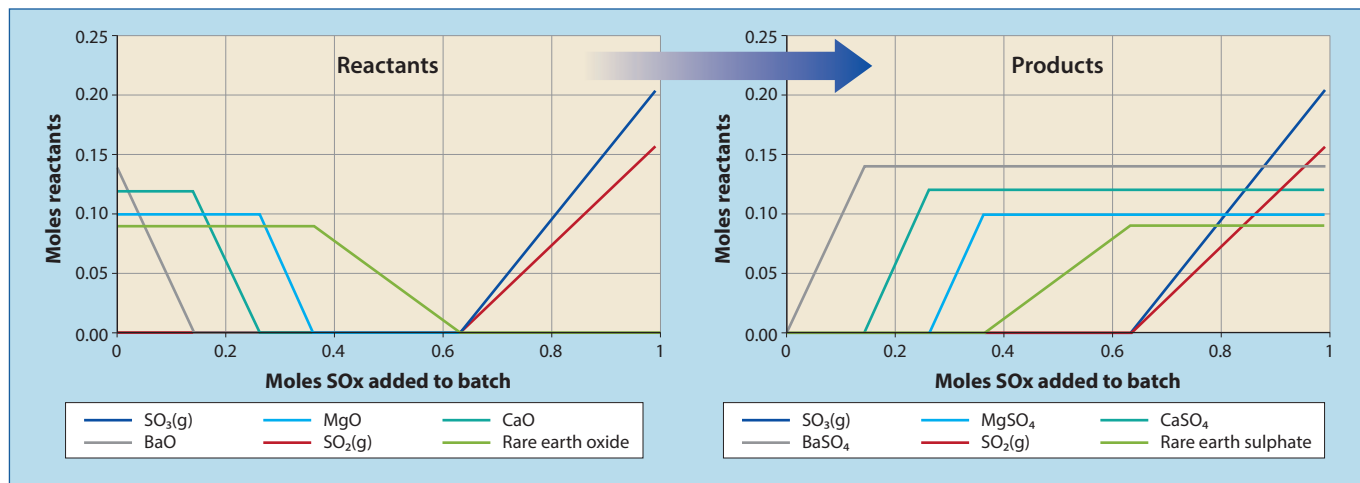


Figure 2 Order of sulphation of vanadium traps. Rare earth is least susceptible to sulphating

earth oxides, which prevents the passivation of vanadium. **Figure 2** shows a thermodynamic calculation performed by BASF where increasing amounts of SO_x are added to a batch containing Ba, Ca, Mg, and rare earth oxides, finding that sulphation occurs in that order. This calculation demonstrates that vanadium traps using rare earth are more tolerant to sulphur at regenerator conditions than the alternative alkaline earth oxides that more readily sulphate.

Based upon this finding, BASF commercialised its proprietary Valor rare earth-based vanadium passivation technology with the goal of improving vanadium passivation through increased sulphur tolerance. **Figure 3** shows the results of a study in which a conventional alkaline earth-based V-trap and the rare earth-based V-trap Valor were both exposed to SO_x in laboratory deactivation conditions.

The samples were then analysed for vanadium and sulphur uptake using scanning electron microscopy (SEM) and imaging software for quantification. As seen in Figure 3, the Valor vanadium trap contains significantly less sulphur following the deactivation procedure. It contains noticeably

higher levels of vanadium, confirming that a rare earth-based V-trap is more effective in passivating vanadium because of improved tolerance to sulphur.

The impact on FCC catalyst performance because of Valor can be seen in **Figure 4**. Laboratory cracking evaluations of FCC catalysts deactivated in the presence of metals (3,000 ppm V and 3,000 ppm Ni), one containing a rare earth-based catalyst (Valor) and the other containing an alkaline earth-based catalyst, shows that the catalyst using a rare earth-based vanadium passivation technology maintains significantly higher activity at comparable catalyst-to-feed ratios (cat/oil).

The only difference in these catalyst designs is the vanadium passivator used. Thus, this higher activity can be attributed to improved vanadium passivation technology. This laboratory-scale experiment demonstrated that the improved sulphur tolerance of a vanadium passivator can result in increased activity maintenance in the presence of vanadium contaminant.

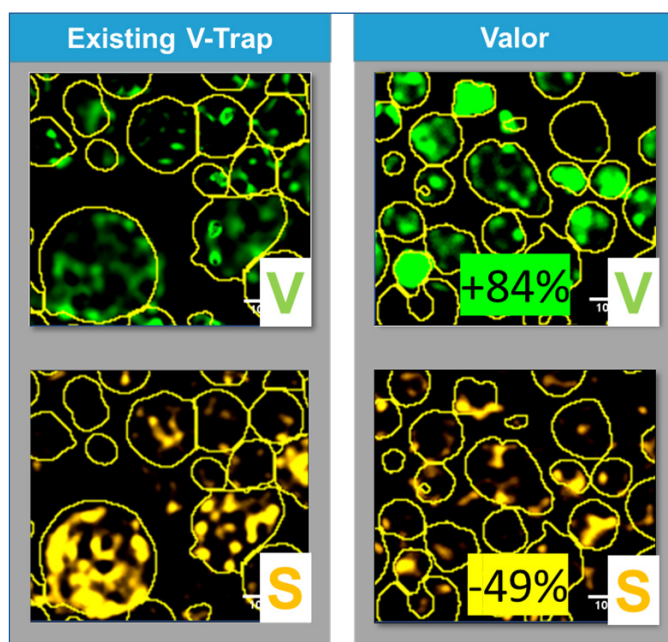


Figure 3 Sulphur and vanadium present the displayed deactivation. Brighter areas indicate higher concentrations

Vanadium passivation in FCC unit trials

While performance in laboratory testing provides insight into strategies for guarding against vanadium contamination

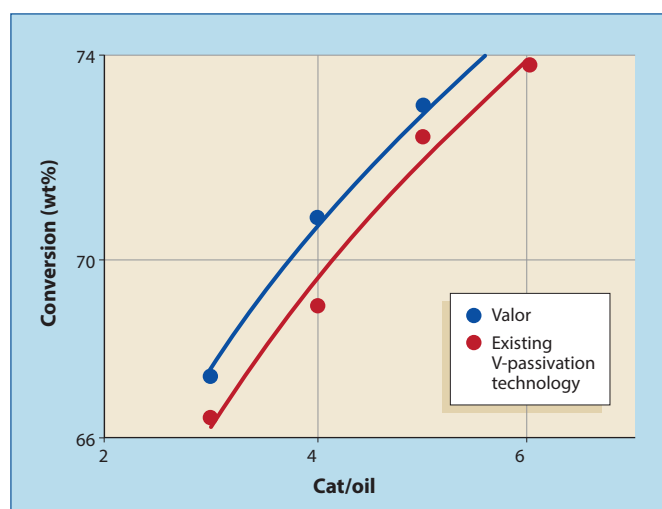


Figure 4 Laboratory testing results of FCC catalyst deactivated to levels of 3,000 ppm V and 3,000 ppm Ni. Cat/oil equals amount of FCC catalyst vs amount of FCC feed

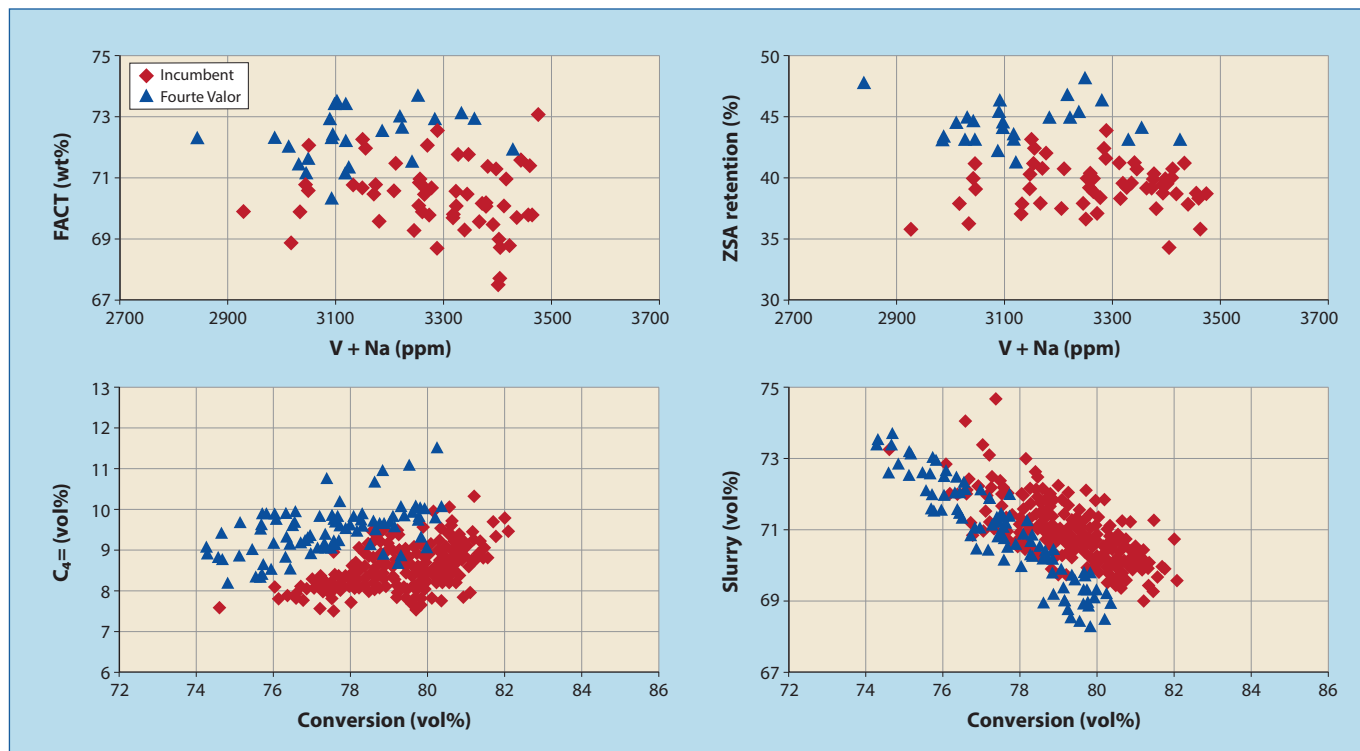


Figure 5 FCC trial results of Fourte Valor catalyst vs incumbent catalyst

in FCC, the true test of a technology is its performance in an industrial FCC unit. The following discussion reviews three trials with different FCC objectives in which novel vanadium passivation technologies were used to improve FCC performance.

The first trial occurred in a North American FCC unit, which processed a feed containing elevated levels of vanadium and sodium. The objective of this FCC case is to reduce slurry and maximise butylenes. To achieve this goal, it was believed that BASF's proprietary Fourte FCC catalyst could better achieve these results compared to the existing catalyst. Given the high amount of vanadium present, it was agreed that advanced vanadium passivation technology would also be needed. Thus, Valor technology was used in the catalytic system. **Figure 5** shows the results from the trial of the new catalyst.

The results clearly indicate multiple improvements to the catalyst system. First, the benefit of improved vanadium passivation can be seen as the amount of zeolite retained by the catalyst compared to fresh catalyst. Zeolite surface area (ZSA) increased by 4-5% at comparable contaminant levels. The impact of this is clearly seen in the Ecat activity of the FCC system following the introduction of Valor, as activity increases 1-2 wt% at a similar contaminant amount.

Fourte catalyst is a technology that uses multiple zeolite frameworks to maximise butylene yields. By using this catalyst in combination with a strong technology to guard against vanadium passivation, the improvements in FCC performance can clearly be seen. The new catalyst technology increased butylene yields by 1-2 vol% and reduced slurry yield by 0.5 vol%, thus helping the FCC unit achieve two major objectives. This trial result was also key, as it demonstrated that the strong vanadium passivation technology can work in parallel with an FCC catalyst designed for the maximisation of light olefins, including butylene.

The second trial is from an Asian FCC that processed resid feed and had a goal to maximise production of propylene while minimising slurry yields. BASF Maximum Propylene Solution (MPS)-Valor was selected as the FCC catalyst to achieve these targets. MPS is designed for maximum propylene yield and selectivity through the optimum use of zeolite-Y, rare earth level, and olefins additive. The Valor technology was necessary given the high levels of vanadium and sodium present in the FCC feed.

Table 1 shows the results from the second trial. Overall, the FCC achieved a 2.6% higher propylene yield, a 0.6% increase in conversion, and a 4.8% decrease in slurry yield compared to the prior catalyst. This was done using lower catalyst additions (8.1% lower), lower riser outlet temperature (20°F lower), and less olefins additive (12% lower Ecat Phosphorous [P]). This is significant as riser outlet temperature (ROT) and olefins additive are two key levers for increasing propylene yield and demonstrate the

Key results from Trial 2			
	Incumbent	MPS-Valor	Change
Feed rate	--	--	-3.9%
ROT, °F	1,000.0	978.6	-2.1%
Slurry recycle, vol%/vol%	1.77	3.14	77.4%
Catalyst addition, lb/bbl	--	--	-8.1%
Ecat vanadium + sodium, ppm	3,926	5,085	29.5%
Ecat P, wt%	1.02	0.90	-12.0%
Dry gas yields, wt%	3.7	3.4	-8.7%
C ₃ =, vol%	13.8	14.1	2.6%
C ₃ =/LPG, vol%/vol%	0.35	0.35	0.6%
Slurry, vol%	5.2	4.9	-4.8%
Conversion, vol%	83.5	84.0	0.6%

Some data omitted at request of refiner.

Table 1

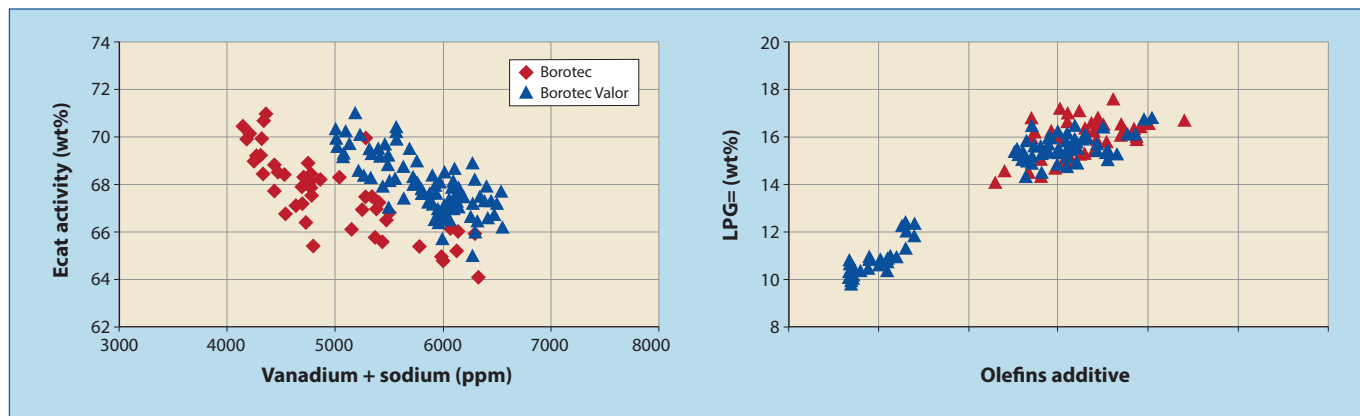


Figure 6 Key results from Trial 3 of Valor technology

impact a catalyst designed for propylene maximisation can make.

While the slightly lower feed rate plays some role in increasing the conversion, it is significant that the Ecat vanadium and sodium levels increased by almost 30%. An increase such as this typically increases catalyst deactivation, lowering the catalyst activity and ultimately lowering conversion in the FCC unit. However, the impact is counteracted using strong vanadium passivation technology.

The final trial example of Valor in an FCC unit took place in a European refinery operating at mild resid conditions. The unit used BASF's Borotec catalyst, which was designed to enable the processing of mild-resid feeds by leveraging boron technology to passivate nickel. Boron is an especially effective way of passivating nickel as it is highly reactive with nickel contaminant, neutralising reacted nickel's ability to produce hydrogen and coke, and has high solid-state mobility – a key necessity since nickel contaminant itself is immobile once deposited on catalyst. The FCC previously held an objective to increase the yield of LPG olefin products, so a reduction in the rare earth on zeolite of the catalyst occurred.

The rare earth change achieved the desired objective but resulted in reduced catalyst activity, as expected. This third trial describes the decision to add Valor vanadium passivation technology to the catalyst system to improve catalyst activity through better vanadium tolerance and, therefore, increased zeolite retention, without losing the benefit gained from increased LPG olefin production.

Figure 6 shows the results of the catalyst trial using Valor compared to the previous catalyst. At comparable metals levels, the catalyst system using Valor noticeably increased the activity of the catalyst system (Ecat activity vs vanadium and sodium). A second, equally important result of the trial is seen in the graph of LPG olefins yield vs olefins additive loading. The two trial catalysts show the same production of LPG olefins product at comparable olefins additive levels. Thus, this demonstrates once again that selecting the proper vanadium passivation technology can result in improved catalyst activity without altering the inherent product flexibility of the FCC catalyst.

Conclusion

Dealing with vanadium in feed continues to be one of the most important challenges for FCCs. It is one of the most

common contaminants found in FCC feeds, leading to losses in catalyst activity and increased coke and dry gas. Furthermore, operational measures to counteract these challenges can be expensive or limited by unit constraints. It is not expected that vanadium or the associated challenges will go away as the refining industry continues to face pressure to operate flexibly and profitably. Thus, optimising an FCC catalyst system through vanadium passivation remains a key need for the present and the future.

This and prior work show that more traditional vanadium passivation technologies can be highly reactive with SO_x found in FCC regenerators. This then impedes the ability of the traditional trap to react with and passivate vanadium contaminant. However, the design of a more sulphur-tolerant vanadium trap is possible. Multiple experimental and in-unit trials have shown that the inclusion of a more sulphur-tolerant technology with FCC catalyst improves the catalyst tolerance to vanadium and that vanadium tolerance improves a refiner's ability to reach a variety of goals.

Trial 1 showed Valor + Fourte catalyst worked well together to preserve catalyst activity, enabling a reduction of slurry and an increase in butylenes yield. Trial 2 demonstrated that Valor + MPS technology led to increased FCC propylene yields using a lower ROT and less olefins additive despite higher levels of vanadium. Finally, Trial 3 described a case in which the FCC catalyst system did not change, but Valor led to increased activity without changing catalyst selectivity. Significant evidence from experimental work and in-unit trials should give FCC operators confidence that the right vanadium passivation technology can help FCCs achieve their goals.

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