DUPONT CLEAN TECHNOLOGIES

MECS® advanced catalysts help manage and reduce sulphuric acid plant emissions

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atalyst is at the heart of all sulphuric acid plants and plays a critical role in plant performance. This article provides an overview of the specific design features of two new types of MECS® sulphuric acid catalyst developed by DuPont Clean Technologies (DuPont), XLP-310 and SuperGEAR™, and explains how these more advanced catalyst types can be applied to reduce emissions or increase the capacity of a sulphuric acid plant.

When asked about key challenges, sulphuric acid plant operators invariably name three issues:

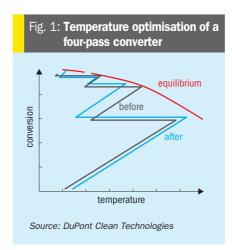
- operational targets run-times that are as long as possible and start-ups that are as fast as possible;
- emissions control or improvement;
- economic factors aligning the objectives above with the economic reality: running the plant at the highest possible capacity while consuming as little energy as possible.

The DuPont Clean Technologies R&D team keeps all three challenges in mind when developing new and improved types of catalyst. Although there are many factors which impact catalyst performance, formulation and shape are two of the key considerations in the design of advanced new catalyst.

Impact of catalyst formulation on conversion

Catalyst is composed of alkali metal, vanadium salts and a diatomaceous earth support. Under reaction conditions, molten alkali metal vanadium pyro-sulphates are formed. These molten salts are supported within the pore structure of the diatomaceous earth. The accepted mechanism for sulphur dioxide oxidation to form sulphur trioxide is a catalytic redox cycle that involves V5+ and V4+ species in the supported liquid phase. The composition of active salts in the liquid phase, as well as accessibility to those salts by the gas stream, plays a large role in the activity level of the catalyst.

In addition to catalyst activity, conversion is impacted by many factors including, but not limited to, gas composition and inlet temperature to each pass,



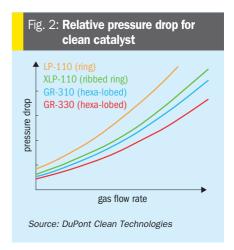
catalyst volume and converter design. In some cases, temperature optimisation alone can allow plants to reach their emission goals. Fig. 1 shows the typical profile of a four-pass converter (before and after temperature optimisation) and illustrates that, ultimately, the conversion of SO_2 to SO_3 is limited by the equilibrium curve.

Traditionally, many plants have added caesium catalyst, which allows for lower operating temperatures and therefore a closer approach to equilibrium, to the fourth pass of their converter in order to reach their desired emission levels. However, thanks to advances in catalyst shape and formulation, many plants can now reach their emission goals without the addition of caesium catalyst through application of more active catalyst in upstream passes of the converter.

Benefits of advanced catalyst shape

For a nominal pellet size, pressure drop in the converter is largely determined by catalyst shape. Ten years ago, DuPont developed the MECS® GEAR® catalyst, which has a unique hexa-lobed ring shape. The new shape created an increased spacing between the rings and thus allowed the gas to pass through the catalyst bed more easily than was possible with traditional ring-type catalysts (see Fig. 2). That not only means a lower pressure drop but also translates into energy savings, as less power is required to operate the main blower.

Dust handling is another factor regulated by the catalyst shape. Most of the dust that

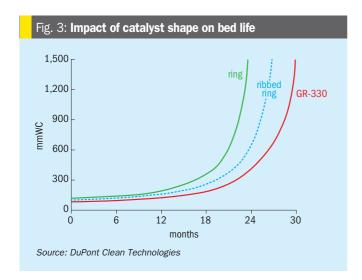


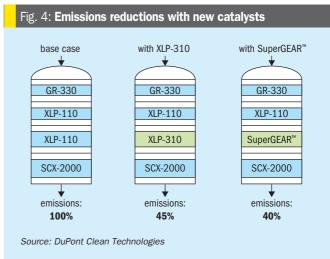
enters the converter is collected in the first pass. If the dust collects at the top of the bed, the pressure drop across the bed will build up faster, which results in shorter runtime between shutdowns. The shape of the MECS® GEAR® catalyst was designed to allow dust to penetrate throughout the bed instead of accumulating at the top. In this way, more dust can be collected before it starts to block the gas flow and cause an increase in pressure drop. The net result is that operators can extend the time between maintenance shutdowns. Fig. 3 illustrates the expected bed life when using different catalyst shapes.

Finally, catalyst shape and the geometry of the individual lobes determine the way in which rings nest into each other and therefore decide the total catalyst surface area per volume of catalyst. The greater the surface area, the greater the interaction of the gas molecules with the catalyst and the higher the final activity. This is exactly what the MECS® GEAR® shaped catalyst set out to achieve, hence its name: GEAR – Geometrically optimised, Enhanced surface area for Activity improvement and Reduced pressure drop.

Latest catalyst advances increase activity

The most recently developed MECS® SuperGEAR™ and XLP-310 catalysts are based on an innovative, improved formulation in combination with the existing ribbed and hexa-lobed ring shapes to ensure pressure drop and dust handling





levels are maintained. The enhanced formulation translates into significantly higher activity levels than the previous generation of catalyst. The volume-based activity of the XLP-310 is more than 50% higher than conventional ribbed ring catalyst and the volume-based activity of the MECS® SuperGEAR™ hexa-lobed catalyst is 65% higher. Performance of both XLP-310 and SuperGEAR™ has been proven through numerous installations in the field.

Benefits of improved activity in an existing plant

Selective addition of the catalyst to critical passes can lead to dramatic results. Plant emissions can be reduced while holding capacity steady, or plant capacity can be increased while maintaining the same emission levels. In some cases, plants may choose to lower emissions to reduce reagent costs of downstream scrubbers or to comply with new environmental regulations. Or they may expand capacity to increase production of finished goods from other parts of their site. Of course, it is only possible to improve plant capacity to the extent that other plant bottlenecks or the hydraulic limit of the blower allow.

Another way of looking at the performance of these advanced catalysts is to consider catalyst loading versus conversion. The same loading of catalyst in the bed can provide a higher conversion, or the same conversion may be obtained with a lower loading. As with all major revamps, DuPont uses its proprietary design software for MECS® catalyst to provide customers with achievable improvement levels based on current operating conditions.

Table 1: Results of catalyst replacement on capacity and emissions

	Year 1		Year 4	
Relative capacity	1.00		1.12	
Relative emissions, ppm	1.0		0.4	
	Catalyst	Per pass conversion, %	Catalyst	Per pass conversion, %
Pass 1	XLP-110	56.5	GR-330/XLP*	60.7
Pass 2	XLP-110	61.1	XLP*	61.2
Pass 3	XLP-110	55.0	XLP-310	65.7
Pass 4	XLP-110	91.9	XLP-310	95.2
Cumulative conversion	99.5%		99.8%	

^{*} mix of XLP-110 and XLP-310

Source: DuPont Clean Technologies

The new MECS® XLP-310 catalyst

Although MECS® XLP-310 may be used in any pass, maximum benefit is derived when it is used in converter passes 2 and 3, as well as in pass 4 if there is no caesium. Fig. 4 provides a comparison with a standard XLP-110 catalyst and MECS® SuperGEAR® catalyst. As can be seen in the scenario shown, complete replacement of XLP-110 with XLP-310 in pass three, with no modifications to passes 1, 2, or 4, has the potential to dramatically reduce emissions.

The advanced MECS® SuperGEAR™ catalyst

The new MECS® SuperGEAR $^{\mathbb{N}}$ catalyst combines the pressure drop and dust handling advantages of the hexa-lobed ring shape with an improved formulation that provides greater activity. This catalyst was mainly

developed for new plants where use of MECS® SuperGear™ catalyst will optimise the capex versus performance. Although maximum value is achieved in new installations, just as with MECS® XLP-310, MECS® SuperGEAR™ can also be selectively applied in existing converters, allowing for a further reduction in emissions.

Application examples

Achieving conversion goals through XLP-310 without major capex

A DuPont client, operating a very large capacity sulphur burning plant, made the decision to renew the company's commitment to sustainable operation by setting even more stringent emission goals for its plant. At the same time, the company realised that additional capacity would be required in order to support fertilizer production. An evaluation by DuPont

determined that the site could meet its goals by focusing on passes three and four of the converter, and that expensive heat exchanger or converter modifications, as initially feared, were not necessary.

Based on DuPont recommendations, the company gradually upgraded the catalyst in its converter over the course of four years. The upgrades included complete new beds of MECS® XLP-310 in passes 3 and 4, installation of MECS® GR-330 in pass one and a partial installation of MECS® XLP-310 in pass 3. The result was an overall conversion increase from 99.5% to 99.8% and a 60% reduction in emissions, at the same time as an expansion in plant capacity of 12% (see Table 1).

Increasing capacity while reducing pressure drop with MECS® SuperGEAR™

For a planned major plant revamp, one DuPont customer is choosing the superior performance of MECS® SuperGEAR™ over other ribbed catalysts. By using caps of SuperGEAR™ in passes 2 and 3, as well as MECS® SCX-2000 catalyst in pass 4 in

the new converter, the company expects to increase its capacity by approximately 25%, reduce overall pressure drop and maintain conversion. The high activity of SuperGEAR should enable the plant to use 13% lower loading than with standard ribbed catalyst, as well as reduce the expected pressure drop by 13%. Super-GEAR will allow them to save on initial capital costs as well as reduce their operating costs over time.

Viability of catalyst-triggered capacity and emissions improvement

Sulphuric acid plant operators with an existing converter who want to improve emission levels should carry out a full and detailed analysis of their current operations to have a clear understanding of realistically achievable outcomes DuPont uses the MECS® PeGASyS $^{\mathbb{M}}$ analysis system which measures the SO $_2$ conversion of every pass to provide a full picture of the performance of each bed. This data is then evaluated with the help of the MECS® catalyst design program,

which predicts what improvements can be achieved using the newly developed catalysts. Sometimes, the PeGASyS $^{\top}$ analysis shows that a simple adjustment of the converter temperature is sufficient to achieve an improvement in plant performance. PeGASys $^{\top}$ measurements could also reveal if it is not the catalyst that is the root cause of a production issue, but in fact another part of the plant that requires maintenance such as the gas-to-gas heat exchanger.

Conclusion

If all other equipment is functioning correctly, advances in catalyst design and formulation can offer significant capacity and emissions improvements. The choice of options available allows sulphuric acid plant operators to select a catalyst mix that matches their production and emissions objectives at the same time as cutting energy consumption, accelerating start-ups and increasing run-times between shutdowns.