Improving sulfuric acid plant performance with MECS' new GEAR™ catalysts

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Introduction

On December 31st of 2010, MECS, Inc., became a wholly owned subsidiary of DuPont and part of the company's Sustainable Solutions business. The combined resources of MECS and DuPont create an expanded portfolio to enhance the safety, reliability and environmental sustainability of customers' facilities.

MECS has been in the sulfuric acid catalyst business since the 1920s. Over the past 90 years, catalyst has evolved from pellets to energy-saving rings to low-emission cesium-promoted catalyst. As energy savings and environmental concerns create new operational and design challenges for sulfuric acid plants, innovations in catalyst technology can provide the solution. Over the past few years, MECS has designed, developed and tested in laboratory and acid plant operations several new catalyst shapes and formulations. Results from these catalyst evaluations led to significant improvements in shape, dust capacity, pressure drop and activity. As a result of these performance improvements, MECS introduces their next generation of sulfuric acid catalysts known as GEAR™ catalysts. GEAR™ is an acronym to define the following catalyst features:

G = Geometrically Optimized
E = Enhanced Surface Area
A = Activity Improvement
R = Reduced Pressure Drop

The GEAR™ family of catalyst products can improve sulfuric acid plant performance by saving energy, extending operating time, lowering SO_2 emissions and increasing acid production.

This article presents the findings of acid plant and laboratory evaluations leading to the new line of GEAR™ catalysts. Based on comparisons with MECS XLP-220 and XLP-110 catalysts, advantages of the GEAR™ catalysts will be demonstrated. Fig. 1 depicts some of the shapes in the new MECS sulfuric acid catalyst portfolio including the new GEAR™ catalyst (13-mm GR-330).

Results

Catalyst Prototype Development

As is often the case in scientific discovery, it takes a few trials to reach the desired results. The development of the GEAR™ catalyst products took several years and a few different prototypes to produce a catalyst family with the desired characteristics.

A plant trial provided valuable information regarding pressure drop and dust handling capability of the improved MECS catalyst. A bed of 13-mm catalyst prototype was placed in the first pass of a small sulfur-burning sulfuric acid plant and run for 27 months at the operating conditions shown in Table 1.

Operating condition	Value
Converter diameter	9.5 ft
Production rate	130 STPD
Pass 1 GR-330 prototype volume	4200 L
Gas strength	8.9 to 9.5 % SO_2
Inlet temperature	411°C (772°F)

Table 1 Operating conditions for the catalyst GR-330 prototype

PeGASyS testing that was done when the catalyst was first charged and at the conclusion of the pass one trial confirmed the catalyst performance. Clean bed pressure drop was measured at four in W. C. After 27 months of operation, the pressure drop in pass one was 12 in W. C. The pressure drop build-up was fit to MECS' proprietary ash pressure drop build-up model showing a result comparable to 15-ppm ash content in the sulfur feed. In contrast, the pressure drop of XLP-220 catalyst in pass one of this plant started out at seven in W. C. and reached 25 in W. C. in 18 months. Fig. 2 shows these pressure drop build-up curves as a percent of clean bed pressure drop. The dust model results show that the larger shape, the GR-330 prototype, extends the operating time by at least eight months, which is a 40 percent longer run time.

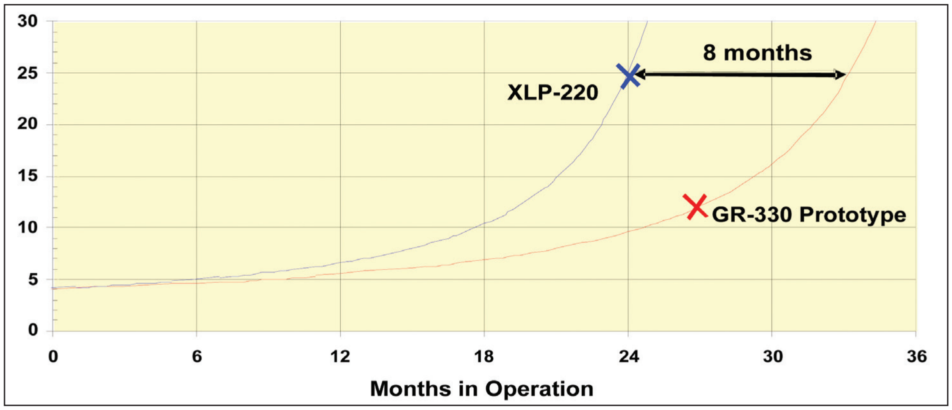

Fig. 2 Predicted pressure drop build-up

Fig. 1 MECS sulfuric acid catalyst shapes, left to right, new 13-mm GEAR™ Hexa-Lobed Ring, 12-mm XLP Ribbed Ring, 10-mm Ring and 6-mm Pellet

To further test the performance of the new GEAR™ catalyst, Southern States Chemical installed the prototype in the first pass at its Wilmington, N.C., plant. "The catalyst has performed with low initial pressure drop and essentially no pressure drop build," said Bryan Beyer, Acid Operations Manager at Southern States Chemical. "We also installed super cesium SCX-2000 in our fourth pass to meet our SO_2 emissions. We have been very impressed with the low SO_2 emissions from the plant, which have been measured to be under half our requirement," said Beyer.

A more active "GR formulation" is another feature developed for the GEAR™ catalysts. To evaluate this formulation with respect to catalyst "stickiness" and activity sustainability, a two-year plant trial was employed. Four 36-inch deep cylindrical sleeves were filled with XLP-shaped (12-mm ribbed ring) catalyst containing this new, more active formulation. The sleeves were placed in the four quadrants of pass one of a large sulfur-burning sulfuric acid plant and operated under the conditions shown in Table 2. Two additional sleeves of standard production XLP-220 catalyst were also placed in pass one.

Operating condition	Value
Converter diameter	42 ft
Typical plant production rate	3600 STPD
Gas strength	11.5 % SO_2
Inlet temperature	428°C (802°F)
Sleeve diameter	0.67 ft
Sleeve length	3.0 ft
Pass 1 GR-formulation-prototype sleeve volumes	30 L
Sleeve distances from bed center	21 ft
Sleeve operating time	24 months

Table 2 Pass 1 catalyst sleeve operating conditions within a converter

After 24 months of operation, the sleeves were recovered, inspected for relative "stickiness" with respect to the entrained dust, and sieved to separate the dust from the catalyst. Four zones consisting of different bed depths of catalyst were evaluated from each sleeve to determine where the dust accumulated. As expected, the new "GR formulated" catalyst performed comparably to traditional "XLP formulated" catalyst, showing analogous levels of dust at the different sleeve depths and free from surface crust formation.

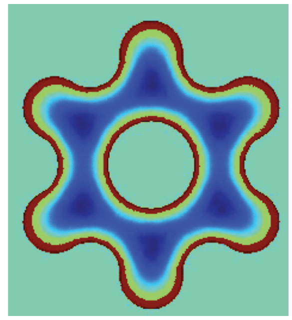

Fig. 3 SO_2 concentration gradients for GEAR™ catalyst. Cross-section at 475 degrees C and 11.0 percent SO_2.

Catalyst activity of the "GR formulation" catalyst sleeve samples was determined for each of the zones. As expected, the high dust zones at the top of the sleeves showed the greatest reduction in activity after two years of operation as measured by the differential conversion of SO_2. In the lower three zones of the four sleeves, the "GR formulation" catalyst showed a higher activity level relative to traditional MECS catalysts following two years of operation and was superior to XLP-220 catalyst in maintaining its overall activity level.

GEAR™ catalyst features

The GEAR™ catalyst hexa-lobed ring shape evolved from both computational and comparative small pilot plant scale results on five different ribbed ring catalyst shapes. The computational results provided relative catalyst effectiveness as a function of each of these catalyst shapes. Fig. 3 depicts SO_2 concentration gradients (Comsol Multiphysics Finite Element Modeling) for the GEAR™ shape indicating good gas penetration into the core of the catalyst from the outer and inner surfaces.

Pilot plant scale (20 to 30 L) catalyst volumes afforded comparative pressure drops and kinetic reaction rates for each of these five catalyst shapes. From these comparative tests, the GEAR™ hexa-lobed ring shape was chosen because it showed the best set of attributes. Table 3 highlights the features of MECS' new GEAR™ catalyst. Note that

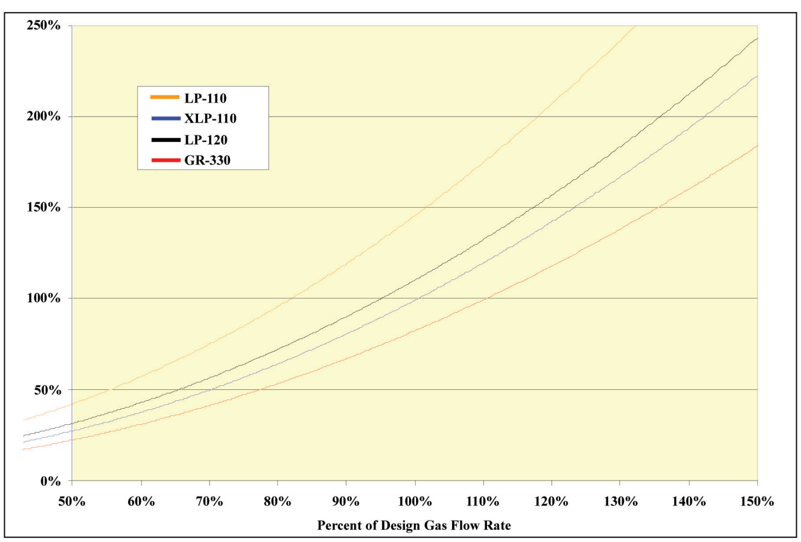

Fig. 4 Relative pressure drop for LP-110, LP-120, XLP-110 and GR-330 catalysts

Fig. 5 Random catalyst packing for GR-330

the GEAR™ catalyst comes in two sizes, providing the best balance of pressure drop and activity for various plant operating conditions.

Catalyst	GR-330	GR-310
Nominal diameter	13 mm	12 mm
Formulation	Advanced	Advanced
Ignition temperature range	350-360°C (662-680°F)	350-360°C (662-680 ° F)
% lower pressure drop than XLP	Up to 25	Up to 10

Table 3 GEAR™ catalyst features

Advantages of the GEAR™ catalysts are demonstrated in the next two sections. Several examples compare the performance of GEAR™ catalyst to XLP catalyst.

Energy savings and extended operating time

From the GR-330 prototype dust build-up results shown in Fig. 2, the pressure drop difference between GR-330 and XLP-220 is likely to widen as dust accumulates on the catalysts over time. These results indicate GR-330 should provide a greater energy savings over time in both pressure drop and extended operating time.

The optimization of the GEAR™ catalyst shape resulted in a lower pressure drop catalyst. One at a time, each of the catalysts in MECS' portfolio were packed into a six-inch vessel and the pressure drop was measured as a function of volumetric flow rate over the entire range of gas flow spanned by the Ergun equation (Ergun, 1952). With temperature and pressure recorded over the entire flow range (0 to 1000 SLPM), the Ergun k1 and k2 coefficients were fit by regression of the pressure drop values. Fig. 4 displays the relative pressure drop against the percent-design gas flow rate for LP-110, LP-120, XLP-110 and GR-330 catalysts. The pressure drop of GR-310 catalyst is not shown in Fig. 4 for clarity purposes.

GR-330 catalyst has up to a 25 percent lower clean pressure drop and GR-310 has nominally 10 percent lower clean pressure drop compared to original XLP catalyst. The reduction in pressure drop results in energy savings for a new or an existing sulfuric acid plant. Alternately, for a new plant design, the pressure drop could remain the same as with XLP catalyst, but the converter diameter could be reduced which lowers the initial capital cost.

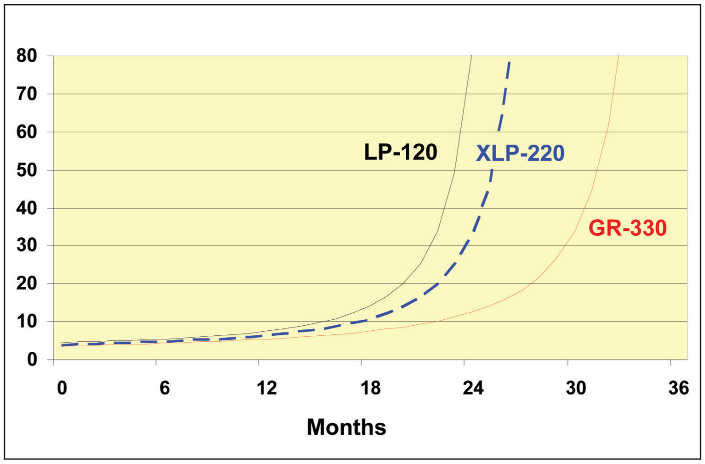

Fig. 6 Estimated pressure drop build-up in a sulfur-burning plant

The pressure drop advantage of GEAR™ catalyst can be more clearly shown by calculating the energy savings. A 3300 STPD sulfur-burning 3X1 IPA acid plant with 11.5 percent SO_2 gas strength to pass one was used for this example. Table 4 shows the pressure drop savings achieved using GEAR™ catalyst compared to XLP. With Florida electricity costs estimated for industrial use at $0.10/kWh (U. S. Energy Information Administration, 2010), the resulting savings from utilizing GEAR™ catalyst equates to $20,000 per inch of pressure drop saved.

Condition	Value
Production rate	3300 STPD
Pass 1 gas strength	11.5 % SO_2
Gas velocity to pass 1	100 SLFM
GR-310 catalyst pressure drop savings vs. XLP	13%
GR-330 catalyst pressure drop savings vs. XLP	21%
Estimated electricity cost	$0.10 / kWh
Estimated annual savings	$20,000 / in W.C.

Table 4 Estimated savings for a full converter of GEAR™ catalyst in a 3300 STPD 3X1 IPA acid plant

The GEAR™ catalyst geometry improves catalyst spacing in the converter. Evidence for this improved spacing comes from comparative pressure drop curves for the GEAR™ catalysts compared to other MECS catalyst shapes. The random packing of the GEAR™ catalyst is shown in Fig. 5.

The new hexa-lobed ring shape of the GEAR™ catalyst also improves dust handling. Given the same dust loading, the pressure drop will rise more slowly over time with GEAR™ catalyst than with XLP catalyst. GR-330 has superior dust handing capability, while GR-310 has better dust handing capability compared to XLP catalyst. Often the operating time between catalyst screenings is limited by the capacity of the main compressor. The GEAR™ catalyst will lengthen the time necessary for the main compressor to reach its capacity, thus increasing the operating time between scheduled turnarounds. Fig. 6 shows the estimated pressure drop build-up of a sulfur-burning plant with a typical dust loading. With a dirty pressure drop limit of 32 inches W.C., the campaign time, in this case, is extended from 24 to 30 months using GR-330 catalyst instead of XLP-220.

Lower SO_2 emissions and increased acid production

The combination of enhanced surface area and activity improvement conferred by the advanced formulation and unique hexa-lobed ring shape reduces the required catalyst volume. Although both GR-330 and GR-310 catalyst will provide process improvements, the GR-310 catalyst is the more active of the two products. If the gas strength remains constant and the GR-310 catalyst volume is adjusted to meet the same emissions as the XLP catalyst, then the GR-310 catalyst will require a nominal 10 percent lower catalyst volume. For a new sulfuric acid plant design, the converter size, and thus the capital investment, could be reduced due to the lower required catalyst volume with GEAR™ catalyst.

For the same catalyst volume, the GR-310 catalyst can also reduce emissions or increase the plant's sulfuric acid production compared to XLP catalyst. If the volume of GR-310 catalyst is kept the same as XLP catalyst, then the increased catalyst activity of the GR-310 catalyst results in up to 25 percent lower emissions for a given gas strength, depending upon the target emissions level. Alternatively, for a given catalyst volume, using GR-310 catalyst and increasing the gas strength can facilitate up to 15 percent higher plant capacity with the same SO_2 emissions. For the lowest overall emissions, use of SCX-2000 cesium catalyst in the final pass or passes is recommended.

The GR-330 catalyst also reduces emissions or improves sulfuric acid production, but to a lesser degree than the GR-310 catalyst. If the gas strength remains constant, GR-330 catalyst meets emissions equal to XLP catalyst, but with a nominal five percent lower catalyst volume. When the catalyst volume is the same as XLP, improved activity in GR-330 catalyst means up to 10 percent lower emissions or up to a five percent increase in plant capacity. Again, SCX-2000 is recommended in the final pass or passes for very low emissions designs.

To illustrate further the SO_2 emissions reduction afforded by the GEAR™ catalyst, four catalyst design cases were considered for a new 3X1 IPA sulfur-burning plant. Table 5 summarizes the four cases that vary by catalyst type and pass four inlet temperature. Catalyst loading remained constant for all of the cases in this comparison. Compared to XLP catalyst, use of GEAR™ catalyst offered 20 percent lower SO_2 emissions. The plant SO_2 emissions for the design with GEAR™ catalyst and SCX-2000 were 65 percent lower than the XLP catalyst design. For ultra-low emissions of 65 ppm, SCX-2000 was used in both the third and fourth passes with GEAR™ catalyst in the upper passes.

Basis: 11.5% SO_2 3X1 IPA Sulfur-Burning Plant				
	Case 1	**Case 2**	**Case 3**	**Case 4**
Pass 1	XLP-220	GR-330	GR-330	GR-330
Pass 2	XLP-110	GR-310	GR-310	GR-310
Pass 3	XLP-110	GR-310	GR-310	SCX-2000
Pass 4	XLP-110	GR-310	SCX-2000	SCX-2000
Pass 4 inlet temperature	425°C (795°F)	420°C (790°F)	390°C (735°F)	390°C (735°F)
Overall conversion	99.812%	99.849%	99.935%	99.953%
SO_2 in stack	260 ppmv	210 ppmv	90 ppmv	65ppmv
Emissions reduction	0%	20%	65%	75%

Table 5 Emissions comparison for XLP and GEAR™ catalysts

MECS catalyst product portfolio

As shown in Table 3, two new GEAR™ catalysts have been added to the MECS catalyst product portfolio. Both products are suitable for use in all converter passes. Catalyst screening trial tests of the GR-330 and GR-310 catalysts showed these products to have the same durability and low screening losses as XLP-220 and XLP-110.

Additionally, the LP-110 formulation has been enhanced to create a new LP-310 catalyst product with the same ring size and shape as LP-110 but in a more active formulation. The LP-310 catalyst can reduce SO_2 emissions or increase acid production compared to LP-120, LP-220 and LP-110 in lower velocity converters.

MECS' revamped product portfolio is shown in Table 6. The new products are highlighted in red.

Hexa-Lobed Rings	Ribbed Rings	Rings	Pellets	Cesium
GR-330	XLP-110	LP-310	T-11	SCX-2000
GR-310	XLP-220	LP-110		XCs-120
		LP-120		Cs-110
		LP-220		

Table 6 MECS new catalyst product portfolio

The GEAR™ catalyst affords several new design options, each with unique benefits. For the lowest pressure drop and maximum extension in the production cycle, GR-330 will be used throughout the converter. A design with GR-310 throughout the converter provides the highest conversion performance and an extension in the production cycle. A combination of GR-330 and GR-310 in the converter will result in a significant improvement in conversion, a reduction in the pressure drop and an extension in the production cycle.

Conclusion

As the data in this article has shown, GEAR™ catalysts provide a range of benefits for improved acid plant performance: energy savings, extended operating time, lower SO_2 emissions and increased acid production. Plants with lower velocity converters similarly can benefit from increased acid production or lower emissions through use of the LP-310 product.

Improved GEAR™ catalysts are the latest addition to MECS' portfolio of products for the sulfuric acid industry. MECS has technologies in this industry that include sulfuric acid plant processes, heat recovery systems for sulfuric acid plant processes, wet gas scrubbing, mist elimination, air preheating, corrosion resistant metals for sulfuric acid service, engineering and consulting services, and PeGASyS plant analysis. In 2011, MECS now combines these products and services with the world-class sulfuric acid plant knowledge, experience and process safety management of DuPont. MECS is ready to meet customer and technology challenges in the 21st century.

For more information, please contact John Horne of MECS, Inc., at (314) 275-5812 or john.r.horne@mecsglobal.com or visit the company's website at www.mecsglobal.com. ❑