IMPROVING SULFURIC ACID PLANT PERFORMANCE

THROUGH NEW SHAPE & HIGHER ACTIVITY CATALYSTS

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ABSTRACT

A new line of sulfuric acid catalysts called GEAR™ has been developed by MECS, Inc. that offers improved performance to the sulfuric acid industry. These catalysts combine a new low-pressure drop ribbed-ring shape with higher activity for a combination of increased energy savings and lower overall plant SO_2 emissions. Pass 1 plant tests with a prototype of our new shape ran for 27 months during which the pressure drop rose from 4 to 12 in W. C., less than half of the typical pressure drop rise. PeGASyS tests of the plant confirmed conversion performance of the catalyst in pass 1. This paper presents several cases to demonstrate the advantages of these new catalysts.

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 1920's. 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 resolution. 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 catalyst performance improvements, MECS introduces in this paper their next generation of sulfuric acid catalysts known as GEAR™ catalysts.

This paper 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 these GEAR™ catalysts will be demonstrated. Figure 1 depicts some of the shapes in the new MECS sulfuric acid catalyst portfolio including the new GEAR™ catalyst (13-mm GR-330).

Figure 1. MECS Sulfuric Acid Catalyst Shapes Range from (left to right) New 13-mm GEAR™ Ribbed Ring, 12-mm XLP Ribbed Ring, 10-mm Ring, and 6-mm Pellet.

RESULTS

Catalyst Prototypes

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 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.

Table 1. Operating Conditions for the Catalyst GR-330 Prototype.

Converter Diameter, ft.	9.5
Production Rate, STPD	130
Pass 1 GR-330 Prototype Volume, L	4200
Gas Strength, %-SO_2	8.9 to 9.5
Inlet Temperature, ^oC (^oF)	411 (772)

PeGASyS testing that was done when the catalyst was first charged and at the conclusion of the pass 1 trial confirmed the catalyst performance. Clean bed pressure drop was measured at 4 in W. C. After 27 months of operation, the pressure drop in pass 1 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 1 of this plant started out at 7 in W. C. and reached 25 in W. C. in 18 months. Figure 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 8 months, which is 40% longer run time.

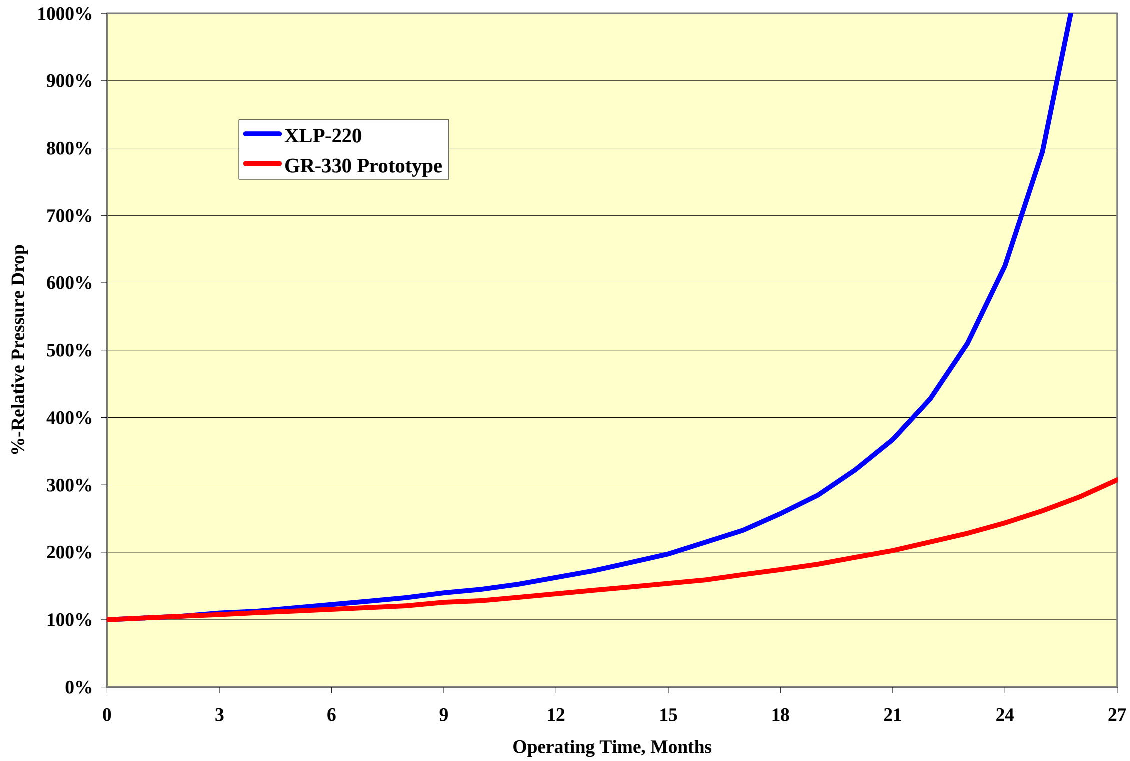

Figure 2. Predicted Pressure Drop Build-up.

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 1 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 1.

Table 2. Pass 1 Catalyst Sleeve Operating Conditions within a Converter.

Converter Diameter, ft.	42
Typical Plant Production Rate, STPD	3600
Gas Strength, %-SO_2	11.5
Inlet Temperature, ^oC (^oF)	428 (802)
Sleeve Diameter, ft.	0.67
Sleeve Length, ft.	3.0
Pass 1 GR-Formulation-Prototype Sleeve Volumes, L	30
Sleeve Distances From Bed Center, ft.	21
Sleeve Operating Time, months	24

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 "GR" formulation catalyst and the XLP-220 catalyst had comparable amounts of dust at the different sleeve depths. The more active "GR" formulation catalyst, along with the XLP-220 catalyst, was free from any "crusting" from the dust.

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 shape evolved from both computational and comparative small pilot plant scale results on five different ribbed ring catalysts shapes. The computational results provided relative catalyst effectiveness as a function of each of these ribbed catalyst shapes. Figure 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.

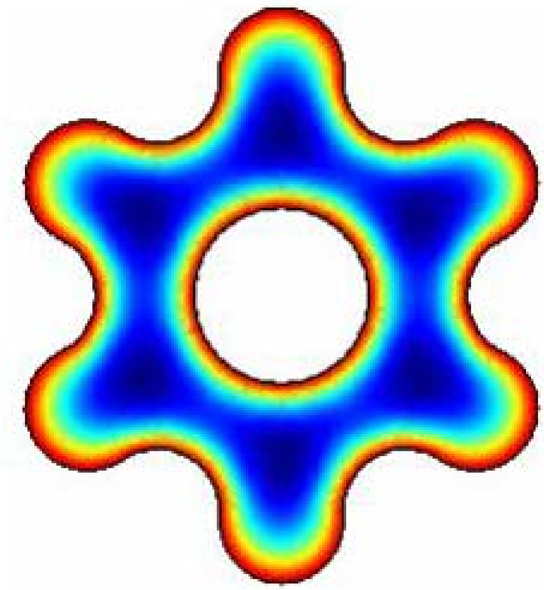

Figure 3. SO_2 Concentration Gradients for GEAR™ Catalyst Cross-Section at 475°C and 11.0% SO_2.

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™ shape was chosen because it showed the best set of attributes. Table 3 highlights the features of MECS' new GEAR™ catalyst. Note that the GEAR™ catalyst comes in two sizes, providing the best balance of pressure drop and activity for various plant operating conditions.

Table 3. GEAR™ Catalyst Features.

Catalyst	**GR-330**	**GR-310**
Nominal Diameter, mm	13	11
Formulation	Advanced	Advanced
Ignition Temperature Range, °C (°F)	350-360 (662-680)	350-360 (662-680)
%-Lower Pressure Drop than XLP	30	15

The GEAR™ family of catalyst products can improve sulfuric acid plant performance by lowering SO_2 emissions, increasing acid production, extending operating time, and saving energy. GEAR^{TM} is an acronym for the following catalyst features:

G = **G**eometrically Optimized
E = **E**nhanced Surface Area
A = **A**ctivity Improvement
R = **R**educed Pressure Drop

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

Lower SO_2 Emissions and Increased Acid Production

The combination of enhanced surface area and activity improvement conferred by the advanced formulation and shape reduces the required catalyst volume. The bar graph in Figure 4 compares the relative volumes of XLP-220/XLP-110 catalyst and GR-330/GR-310 catalyst for the same conversion. If gas strength remains constant and GEAR^{TM} catalyst volume is adjusted to meet the same emissions as XLP catalyst, then the GEAR^{TM} catalyst will require 5 to 15% lower catalyst volume. The trend in Figure 4 shows that GEAR^{TM} is more effective at higher gas strengths than XLP catalyst.

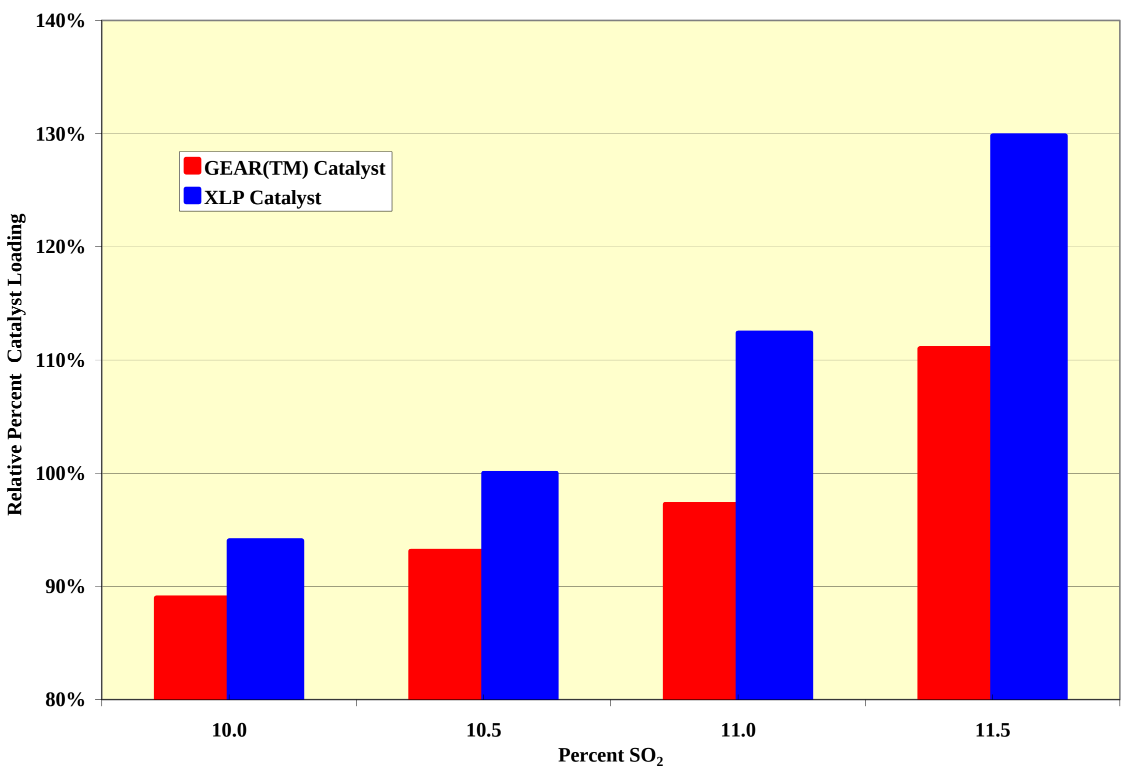

Figure 4. GEAR^{TM} Catalyst Requires Less Catalyst than XLP Catalyst for the Same Conversion.

If the volume of GEAR™ catalyst is kept the same as XLP catalyst, then the increased catalyst activity of GEAR™ catalyst results in 10 to 30% lower emissions for a given gas strength, depending upon the target emissions level. These relationships are shown in Figure 5. Alternatively, for a given catalyst volume, using GEAR™ catalyst and increasing the gas strength can facilitate 5 to 6% higher plant capacity with the same SO_2 emissions. For the lowest overall emissions, use of SCX-2000 in the final pass or passes is recommended.

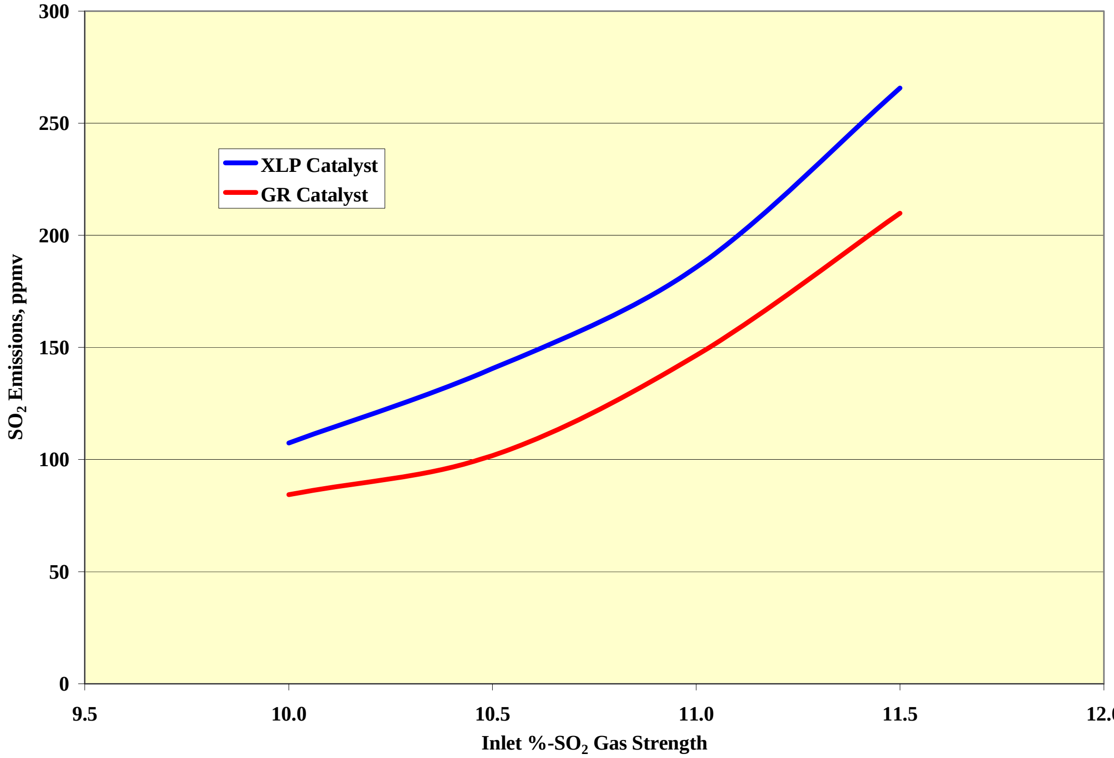

Figure 5. GEAR™ Catalyst Reduces SO_2 Emissions Compared to Same Volume of XLP Catalyst.

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 4 summarizes the four cases that vary by catalyst type and pass 4 inlet temperature. Catalyst loading remained constant for all of the cases in this comparison. Compared to XLP catalyst, use of GEAR™ catalyst offered 20% lower SO_2 emissions. The plant SO_2 emissions for the design with GEAR™ catalyst and SCX-2000 were 65% 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.

Table 4. Emissions Comparison for XLP and GEAR™ Catalysts.

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, ^oC (^oF)	425 (795)	420 (790)	390 (735)	390 (735)
Overall Conversion, %	99.812	99.849	99.935	99.953
SO_2 in Stack, ppmv	260	210	90	65
%-Reduction	0%	20%	65%	75%

Energy Savings

From the GR-330 prototype dust build-up results above (Figure 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. Placing either GR-330 or GR-310 catalysts in the lower passes will increase further the annual savings from the pressure drop advantage of these catalysts. 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 Figure 6.

Figure 6. Random Catalyst Packing for GR-330.

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 6-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 k_1 and k_2 coefficients were fit by regression of the pressure drop values. Figure 7 displays the relative pressure drop against the %-design gas flow rate for LP-110, LP-120, XLP, and GR-330 catalysts.

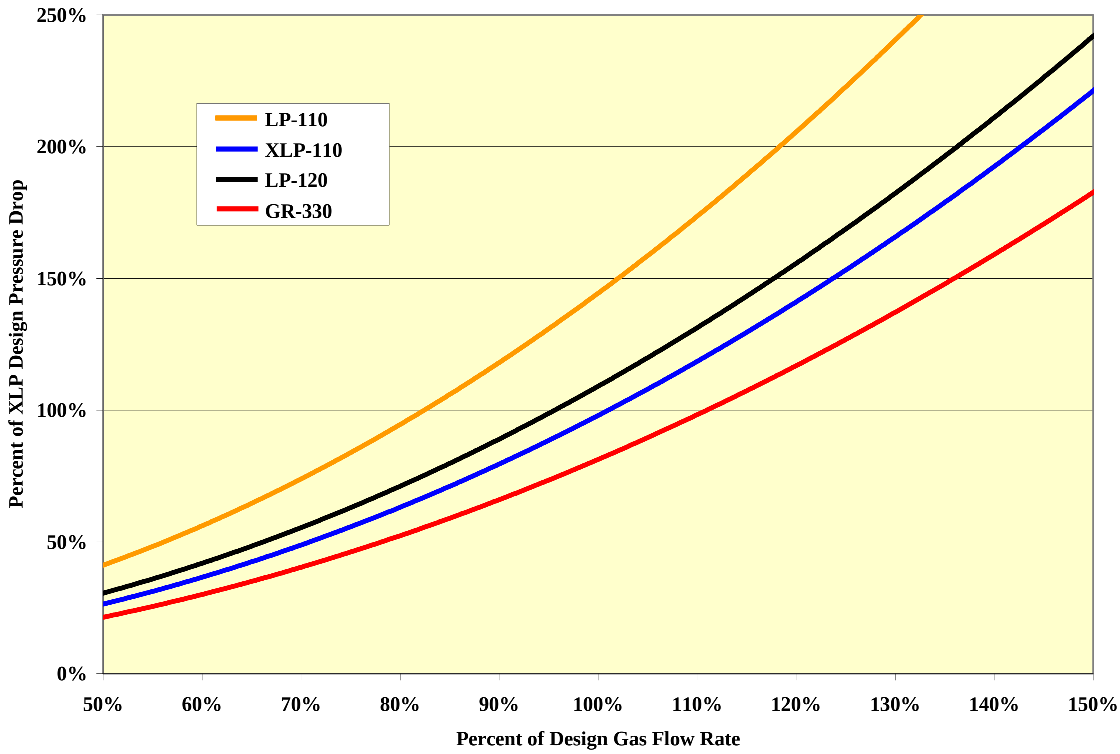

Figure 7. Relative Pressure Drop for LP-110, LP-120, XLP, and GR-330 Catalysts.

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% SO_2 gas strength to pass 1 was used for this example. Table 5 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.

Table 5. Estimated Savings for a Full Converter of GEAR™ Catalyst in a 3300 STPD 3X1 IPA Acid Plant.

Production Rate, STPD	3300
Pass 1 Gas Strength, %-SO_2	11.5
Gas Velocity to Pass 1, SLFM	100
GR-330/GR-310 Catalyst Pressure Drop Savings vs. XLP	15%
GR-330 Catalyst Pressure Drop Savings vs. XLP	30%
Estimated Electricity Cost, $/kWh	$ 0.10
Estimated Annual Savings, $/In W. C.	$ 20,000

MECS Catalyst Product Portfolio

As shown in Table 3, two new GEAR™ shapes have been added to the MECS catalyst product portfolio. 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' new product portfolio is shown in Table 6. The new products are highlighted in red.

Table 6. MECS New Catalyst Product Portfolio.

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

CONCLUSIONS

The GR-330, GR-310 and LP-310 catalysts will be available from MECS starting in the third quarter of 2011. As the data in this paper have shown, GEAR™ catalysts provide a range of benefits for improved acid plant performance: lower SO_2 emissions, increased acid production, extended operating time, and energy savings. 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 edition 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 twenty-first century.

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