MECS® sulfuric acid catalyst: celebrating 100 years of innovation

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Over the past century, the number of sulfuric acid plants operating globally has expanded exponentially. Throughout the 20th century, rapid industrial growth in combination with increasing demand for superphosphate fertilizers led to high demand for the "king of chemicals," sulfuric acid. Today, sulfuric acid is one of the most utilized commodity chemicals in the world with widespread applications in the phosphate fertilizer, non-ferrous metals, chemicals, and oil refining industries. In the early 1900s, the contact process for sulfuric acid production was improved greatly with the development of vanadium-based sulfuric acid catalysts. Previous sulfuric acid manufacturing using lead chamber units or contact processes utilizing platinum catalysts was expensive, unreliable, and produced lower strength acids.

To support its first sulfuric acid plant built in 1917, MECS, Inc. (MECS), then Monsanto, quickly advanced research and development on contact sulfuric acid processes, including the use of vanadium-based catalysts. The research and production facilities for the vanadium-based catalyst were established at the Commercial Acid Company site, then designated as Monsanto Plant "B." In 1925, Plant B produced what was known as the "Monsanto Mass" catalyst, which eventually led to the "Type 210A" (T-210A) commercial product. Fig. 1 shows an example of an indoor acid plant constructed in 1930 by Leonard Construction Co. at the then newly acquired Monsanto Chemical Company plant site in Everett, Mass. The converters at this plant site contained the original T-210A catalyst. Fig. 2 provides an example, ten years later, of a larger outside contact sulfuric acid plant.

Over the next two decades, MECS and Leonard Construction Co. designed, constructed, and provided operations for more than 250 sulfuric acid plants in 30 countries creating a global business with customers for catalyst and acid plant equipment and services. During this time, acid plant sizes grew, and converter designs started to employ a single vessel with ducts connecting the incoming SO_2-containing gas stream and heat exchangers as separate unit operations.

Growth in catalyst production meets needs of the industry

The following decades were marked by rapid growth for MECS. By 1945, MECS had designed 40% of the world's contact sulfuric acid capacity. By the late 1960s, the Plant B site was producing over 1MM liters of catalyst per year. In contrast, today there are plants operating with over 1MM liters in a single converter. This growth in demand led to the eventual move of the Illinois MECS® catalyst production facilities to the Avon site in Martinez, Calif., which started up in 1970. Today, MECS has more than 1,000 sulfuric acid plant licenses and projects worldwide.

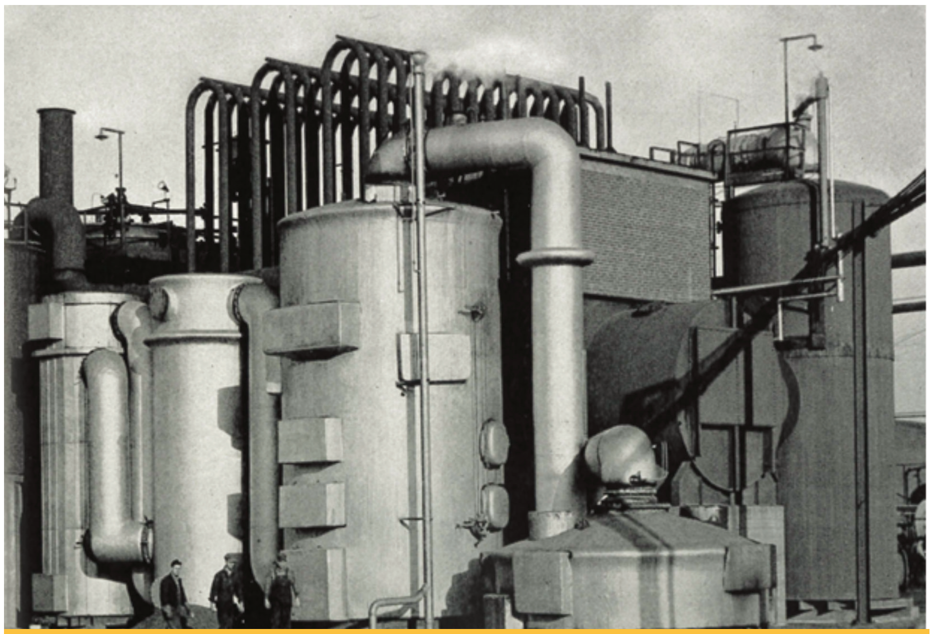

Fig. 2: Outdoor steel vessel design containing converter passes at the Monsanto, Illinois site in 1940.

In addition to growth in demand for catalysts, the science and technology behind the catalyst also grew substantially in the years following the construction of Monsanto's first sulfuric acid plant. The active catalyst formulation was recognized to be in molten salt that melted at reaction temperatures. The key elements comprise alkali metals, vanadium, and sulfate anions in both sulfate and pyrosulfate states. These alkali-vanadium-sulfate molten salts (now often referred to as ionic liquids) were found to function as catalysts for sulfur dioxide oxidation in both bulk and supported forms. The active phase was on predominantly silica-based supports. Supported catalysts soon evolved from pellet to larger ring-shaped catalysts that adapted to the needs of converter designs having higher gas flow rates and sulfuric acid production capacities.

R&D into more energy-efficient catalysts increased starting in the 1970s. In that decade, the energy crisis drove the need

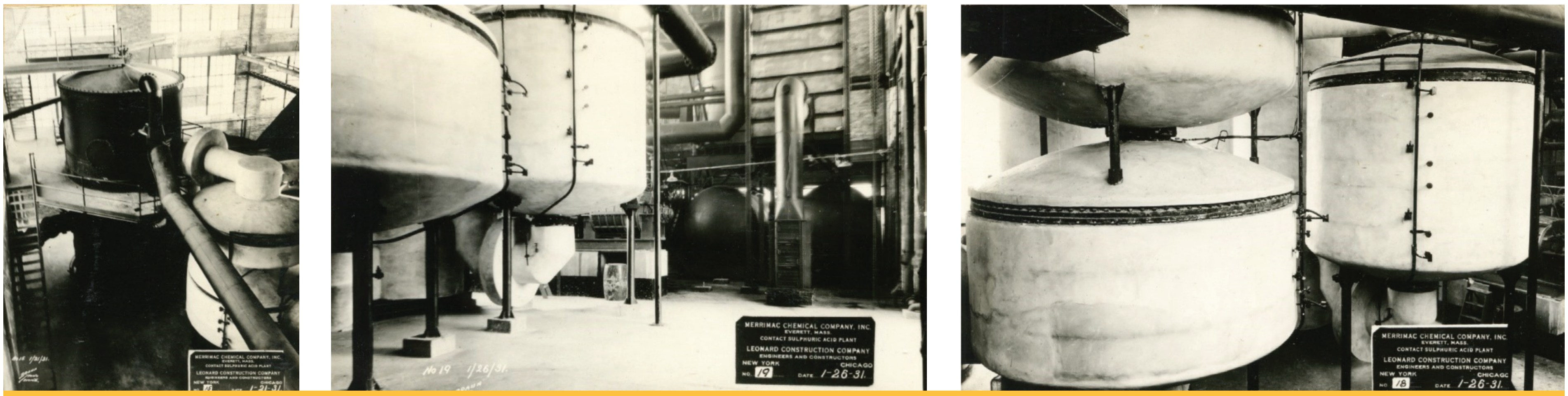

Fig. 1: Acquired by Monsanto Chemical Co. in 1930, the expanded capacity contact unit at the Merrimac Chemical Company plant in Everett, Mass, produced 75 STPD. These indoor units, built by Leonard Construction Co., operated with feed gas supplied by combustion of molten sulfur using contact units filled with T-210A catalyst.

MECS® CATALYST MILESTONES

1925
MECS, Inc. begins producing sulfuric acid catalyst.

1963
T-11 catalyst is originally developed, with improved performance over the original T-210 pellets.

1970
MECS® sulfuric acid catalyst production is moved to the Avon site in Martinez, CA.

1980-1981
Smooth rings LP-120 and LP-110 are brought to market.

1989
MECS starts making its first low temperature cesium-promoted catalyst Cs-110.

LATE 80s
MECS develops the PeGASyS™ *(Portable Gas Analysis System)* program, providing high quality data on the performance of sulfuric acid converters.

2000
MECS introduces the XLP ribbed ring product line with lower pressure drop and higher conversion performance: XLP-110, XCs-120 and SCX-2000.

2009
The MECS® wet sulfuric acid catalyst product line, including WXP-110 and WXC-120, becomes available.

2011
MECS launches the GEAR® family of catalyst products, which includes GR-Cs, GR-330 and GR-310.

2019
MECS begins offering the highly active Super GEAR® and XLP-310 products.

2025
Elessent celebrates 100 years of MECS® sulfuric acid catalyst.

for lower pressure drop style catalysts that led to the MECS® "low pressure" drop LP smooth ring style catalyst products. Unlike the traditional pellet-style catalysts, LP catalysts drastically reduced the pressure drop buildup across the old low-velocity converters. LP catalysts were formulated to minimize screening losses and when combined with higher activity, LP catalysts met the needs of acid plant customers in the early 1980s.

> "The MECS® catalysts we use have proven outstanding with their long lifespan and low screening loss. These characteristics ensure efficient and reliable performance in our operations."
> - Mr. Chen Ziling, Production Director, Two Lions

MECS® sulfuric acid catalyst advances in the 21st century

Over the next decade, MECS continued to optimize the shape of catalysts to minimize energy costs and extend production cycles. A computer-aided ribbed ring catalyst shape was designed in the late 1990s through variations on the outside and inside (die pin) diameter, rib thickness, and rib depth. The resulting "XLP" shape produced a catalyst with significantly better reactor performance than the LP catalysts with higher activity, improved extrudate hardness, and lower pressure drop enabling operation at high gas velocities used in larger acid plants. In the early 2000s, the XLP product line was officially introduced, including MECS® XLP-110, which is now the industry standard with installations in over 450 plants globally.

The development of GEAR® shaped catalysts required a longer development path with parallel field and laboratory testing activities. A prototype of the GR-330 catalyst called "Bigfoot" was produced and installed in the first pass of a sulfur-burning acid plant. The 13-mm Bigfoot catalyst exhibited very good activity over a 27-month testing period with measured pressure drop rising from the fresh value of 4 inches of water column to 12 inches of water column at the end of the test. The results demonstrated that Bigfoot extended operating time by 40% or 8 months more than a typical ribbed ring catalyst. During the field-testing period, laboratory tests compared the hexa-lobed shape to ribbed ring aluminum shapes. Equal volumes of the hexa-lobed and XLP shapes having the same outer diameter were settled in a pressure drop tube, and the pressure drop was measured and fit to the Ergun equation. The combined field and lab testing results led to the emergence of the GEAR® hexa-lobed design as a premium shape. These results justified the commercialization of the GR-330 catalyst, and after a slight formulation enhancement, sales of the new GEAR® catalyst shape began in early 2012.

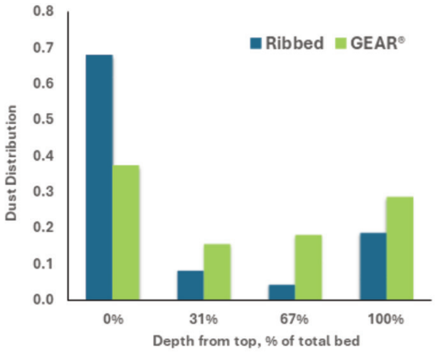

Fig. 3: Comparison of dust accumulation in catalyst bed after three years of operation.

As shown in Fig. 3, GEAR® catalysts demonstrate a marked improvement over ribbed ring catalysts in the ability to let dust filter through the bed. Dust buildup on the top of a catalyst bed leads to a more rapid increase in pressure drop over time, but the specially designed structure of the GEAR® lobes encourages dust to move deeper into the catalyst bed thus slowing pressure drop buildup.

Development of cesium-promoted catalysts

Alongside the push for more energy-efficient catalysts, increasing regulations on clean air, double absorption plant designs, and SO_2 emissions have driven improvements in conversion performance and operational flexibility. Sulfuric acid plants today require ultralow emissions and the ability to start up quickly. Beginning in the 1980s, MECS began developing cesium-promoted catalysts for improved low-temperature performance. Cesium forms alkali-vanadium sulfate salt mixtures that lower the molten salt melting point below 400°C. Cesium-promoted catalysts such as XCs-120 enable sulfuric acid plants to heat converters faster during startup saving critical downtime and reducing the emissions over the dynamic startup period. With lower temperature performance, cesium-promoted catalysts also provide the opportunity for increased conversion in individual beds before reaching the equilibrium conversion limit.

In 1989, MECS introduced its first cesium-promoted product: Cs-110. The catalyst had excellent SO_2 conversion for its time, allowing for acid plant designs with dramatically reduced emissions. As new shapes were developed in later years, improved cesium products XCs-120 and eventually GR-Cs were brought to market. As shown in Fig. 4, using reduced inlet temperatures, cesium-promoted catalysts afford higher conversion performance that continues in the following catalyst beds and ultimately leads to lower SO_2 emissions.

For acid plants seeking ultra-low

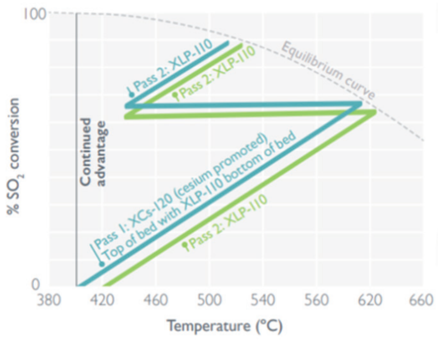

Fig. 4: Advantages of cesium-promoted catalyst on conversion performance.

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emissions, MECS introduced the "super cesium" product SCX-2000 during its namesake year. SCX-2000 was specifically formulated for the final pass of a sulfuric acid plant converter operating with low SO_2 inlet gas concentrations. Under these conditions, highly active catalysts are required to achieve significant conversion of SO_2 to SO_3. Additionally, because of the low gas strength, catalysts capable of low temperature performance are needed. These benefits are displayed in Fig. 5. By reducing the inlet temperature into the final bed from 425°C to 390°C and upgrading to SCX-2000, this customer was able to reduce emissions by 35%.

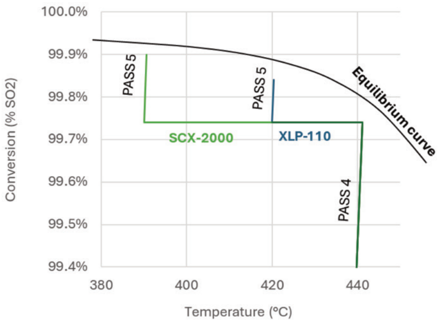

Fig. 5. Comparison of Pass 5 conversion using standard and cesium-promoted catalysts.

Development of high-performance catalysts

Development of SCX-2000 enabled MECS to offer impressive designs for ultra-low emissions performance. However, with the limited availability of cesium raw materials, the market price of cesium started to rise significantly over the next several years. To provide another option for acid plants, particularly for those with less stringent emissions requirements, MECS began work on a series of high-performance catalysts that did not need the high-cost cesium promoter.

Along with the development of GR-330, MECS also produced the GR-310 catalyst. This 12mm diameter option was designed for intermediate passes of the converter to provide continued low pressure drop across the operations, as well as boosting the overall conversion performance. The GR-310 catalyst proprietary formulation took advantage of optimized potassium levels to boost the volume-based activity of the catalyst.

In 2019, MECS went further with the announcement of two new product offerings: XLP-310 and Super GEAR® catalysts. The development of these catalysts demonstrated a significant advance in conversion capabilities with sulfuric acid catalysts. The proprietary formulations provide the most active non-cesium conversion performance in the MECS® catalyst product line.

YEAR	1		2		3		4	
CAPACITY	1.00		1.10		1.10		1.12	
EMISSIONS	1.0		1.07		0.4		0.4	
PASS CONVERSION, %								
Pass 1	XLP-110	56.49	GR-330	61.18	GR-330*	64.90	GR-330*	60.71
Pass 2	XLP-110	61.11	XLP-110	59.82	XLP-110	57.86	XLP-110	61.18
Pass 3	XLP-110	54.97	XLP-110	49.95	XLP-310 / 110	60.10	XLP-310	65.70
Pass 4	XLP-110	91.91	XLP-110	92.16	XLP-310	96.08	XLP-310	95.20
CUMULATIVE CONVERSION, %	99.49		99.50		99.81		99.79	

Table 1. Initial field trial of XLP-310 in a large capacity sulfur-burning plant

Case Studies of MECS® XLP-310

Since its introduction in 2019, XLP-310 has been installed in over 30 plants worldwide and data has been collected confirming its performance capabilities. Using MECS® PeGASyS™ (Portable Gas Analysis System) testing, highly accurate metrics can be collected around the acid plant converters. PeGASyS™ testing incorporates a gas chromatograph diagnostic system and proprietary simulation software to sample, analyze, and optimize converter performance.

Case 1: A study of two existing sulfur burning plants

Initial field trials of XLP-310 included a 4-year study in a sulfur burning plant as shown in Table 1. PeGASyS™ testing was used to monitor the conversion across each bed over each year of the study. In combination with GR-330 in Pass 1, the use of XLP-310 catalyst enabled this acid plant to achieve 99.8% conversion without the use of cesium-promoted catalysts. In a similar application years later, another client upgraded their converter to improve reliability and reduce energy costs. PeGASyS™ testing was used to evaluate the performance before and after the installation of the new converter and upgraded catalyst. The emissions results were confirmed to drop significantly with the installation of XLP-310 catalyst as seen in Table 2. When testing 1 year later, the acid plant was operating at 18% higher capacity with less than 10% additional volume of catalyst. As shown in Tables 1 and 2, both sulfur burning plants reduced emissions by more than half with the installation of XLP-310 in two beds of the converters.

YEAR	1		2	
CAPACITY	1.00		1.18	
EMISSIONS	1.0		0.39	
PASS CONVERSION, %				
Pass 1	GR-330	57.23	GR-330	62.67
Pass 2	XLP-110	54.29	XLP-310	68.28
Pass 3	XLP-110	55.73	XLP-310	63.96
Pass 4	SCX-2000	96.12	SCX-2000	97.49
CUMULATIVE CONVERSION, %	99.68		99.89	

Table 2: Revamp of 3x1 sulfur-burning plant with over 12% SO_2.

Case 2: A new 4x1 metallurgical plant

XLP-310 is a valuable tool for reducing emissions in an existing plant, as well as minimizing the capital costs for new acid plants. In a recent startup of a 5-pass metallurgical sulfuric acid plant, the plant achieved emissions of less than 120 ppm while using XLP-310 in Pass 3 as shown in Fig. 6. The emissions resulted in 99.9% overall conversion which was achieved without the use of cesium in the final beds. Due to the high SO_2 inlet, a cesium cap was used in the first bed to prevent the outlet temperature from exceeding the converter's recommended temperature limits. The performance of the new plant was confirmed through PeGASyS™ testing in addition to standard stack monitoring.

Fig. 6: A new 4x1 metallurigical acid plant with high gas strength.

Case 3: Low temperature third bed conversion in a pilot plant

In addition to PeGASyS™ testing in the field, MECS uses an in-house pilot plant to assess catalysts across a variety of conditions. Testing showed that XLP-310 demonstrated superior performance in a high SO_3 environment typical of a 3rd pass. The boost in this difficult application led to the potential for significant reductions in loading to achieve similar performance. Expanded testing also revealed that the XLP-310 catalyst shows improvements even at sub-optimal temperatures in Pass 3. Typically, for Pass 3 operations without cesium, it is recommended to stay above 430°C inlet to ensure a good "light off" (activation) of the catalyst bed. However, even at temperatures as low as 420-425°C inlet, XLP-310 provides significant enough performance for good operation without the need for a cesium promoter. The comparative performance of XLP-310 and a standard ribbed ring catalyst in Pass 3 at 425°C is shown in Fig. 7.

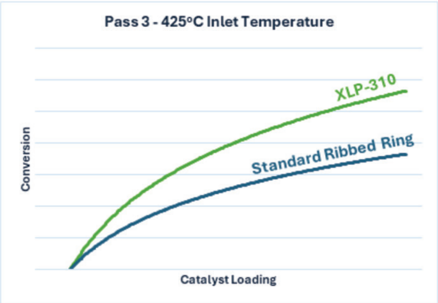

Fig. 7: XLP-310 performance as compared to a standard ribbed ring catalyst in Pass 3 at 425°C inlet.

Conclusion

What began 100 years ago as a vanadium catalyst formulation trial to qualify its use in Monsanto sulfuric acid plants quickly grew to a worldwide catalyst and sulfuric acid plant business. As sulfuric acid plant designs and capacities increased, the catalyst adapted through more energy-efficient shapes and higher performance formulations. With over a century of development, MECS has built a varied product line to address specific acid plant requirements:

- Low-pressure drop GEAR® catalysts to minimize operating costs
- Cesium-promoted catalysts for faster startups and ultra-low emissions
- High-performance catalysts for expanded capacity and high conversion

Customized catalyst design and support are key to meeting the ever-increasing needs of acid plants to improve output, reduce costs, and operate sustainably.

The sulfuric acid catalyst product portfolio from MECS, Inc. is built on a century of research and development. The newest line of products is designed to reduce emissions, minimize pressure drop, and provide operational flexibility across the acid plant production cycle.

For more information, please visit elessentct.com/technologies/mecs/. ❏