

MECS catalyst products and technical services update

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Synopsis

Vanadium-based sulphuric acid catalyst has been utilized to oxidize SO_2 to SO_3 since the early 1900s. This versatile product displaced the expensive and easily poisoned platinum-based catalyst in nearly all applications by the 1930s. MECS has been manufacturing the vanadium-based catalyst since 1925 and today is the leading supplier in the world of sulphuric acid catalysts in a variety of forms. Currently, MECS has worldwide customer/technical support for the catalyst as well as a dedicated catalyst manufacturing plant in Martinez, California. MECS also has a strong technical and research and development programme dedicated to creating new and improved products and services. This paper will describe some of the technical details of vanadium-based sulphuric acid catalysts as well as offering a unique look into how caesium-promoted MECS catalysts can be used in single and double absorption acid plants, and off-gas plants running on irregular gas feeds, to reduce emissions and preheater run times. An update on MECS technical services extended for use in characterizing converter performance is also presented.

Standard catalyst composition

Sulphuric acid catalyst is composed of potassium (K) and vanadium (V) salts supported on a silica (SiO_2) carrier. The silica support is diatomaceous earth (DE), which consists of skeletons of diatoms (microscopic sea creatures); the DE provides the ideal properties for the sulphuric acid catalyst at an acceptable cost. The potassium-vanadium salt mixture actually liquefies under reaction conditions (> 350°C) and forms a molten salt catalyst. The salt formation reaction can be shown as follows:

$$K_2S_2O_7 + V_2O_5 \text{ ——— } K_wV_xS_yO_z\left(\text{molten salt compound}(s)\right)$$

The actual composition of the critical molten salt is still widely disputed; hence, the generic labelling of the salt compound with w, x, y, and z values.

MECS standard catalyst products

MECS is proud to offer a wide variety of standard potassium-promoted catalysts suitable for every application:

The 'XLP' six-lobed, ribbed-ring line of catalysts offer extended surface area and lowest pressure drop and highest conversion performance in all beds of the converter. (Figure 1.)

- XLP-220 (Beds 1 and 2)
- XLP-110 (Beds 2, 3, 4 and 5)

The 'LP' raschig-ring line of catalysts offer low pressure drop, high activity and low fouling rates. LP catalysts have been a standard in the sulphuric acid industry for many years. (Figure 2.)

- LP-120 (Beds 1 and 2)
- LP-220 (Beds 1 and 2)
- LP-110 (Beds 2, 3, 4 and 5)

The 'T' pellet lines of catalysts are for low gas velocity converter designs and where maximum durability is required for lower screening losses. (Figure 3.)

- T-210 (Beds 1 and 2)
- T-11 (Beds 2, 3, 4 and 5)

Factors affecting catalyst life

There are a number of factors that can affect the life of the sulphuric acid catalyst. The catalyst life can be shortened through the following mechanisms:

- *Vanadium loss*—dust accumulation in the bed; iron oxide corrosion products; chlorides in the gas stream; and acid/moisture contact with catalyst
- *Moisture contact*—leaching of the active salts; decreased catalyst hardness
- *Poison*—arsenic (oxide coating of the catalyst)
- *Carrier degradation*—fluorine attack (forms volatile SiF_4); thermal cycling.

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Figure 1—XLP six-lobed, ribbed-ring line of catalyst



Figure 2—LP raschig-ring line of catalyst



Figure 3—T pellet lines of catalysts

Temperature 'memory' effects in catalyst

Over the years, this 'philosophy' of catalyst performance has limited the capabilities of many sulphuric acid plants to optimize the converter performance. Plant operators have hesitated to raise catalyst bed inlet temperatures (with the potential result of increasing conversion) because of fear of 'damaging' the catalyst with respect to lower temperature operation. In general, within a catalyst bed, catalyst 'damage' will only occur if the bed temperature has been at least 100°C higher than the initial operating temperature for an extended time period (> 7 days). The damage that can occur is more physical than chemical in nature. At the high temperatures, the structure of the 'catalyst support' can change with subsequent decrease in surface area. This lower surface area will directly result in reduced catalyst activity at a lower operating temperature. The reaction rate at the higher temperatures is so large that there will be little effect on the overall achieved conversion. Hence, a catalyst that has been operating at 530°C for a long time (for example in the middle of the first catalyst bed) will not perform as well as fresh catalyst when operated at 430°C due to this structural change. Because of this phenomenon, it is therefore suggested that plant operators never move catalyst from the bottom of Bed 1 to the cooler top of the first bed. The same recommendation applies to Bed 2. Catalyst within Beds 3 and 4 can be freely rearranged depending on the convenience of the plant personnel. However, it is recommended practice to always place any fresh catalyst on the top of any bed during normal plant maintenance.

The active ingredients within a sulphuric acid catalyst will vary from bed to bed as the level of SO_3 (a major component of the active molten salt) in the gas stream is dependent on the overall conversion. Also, the SO_2/SO_3 ratio in the gas phase has a large effect on the composition of the active catalyst phase. Because of these chemical 'circumstances', it is recommended that, if necessary, plant operators should always move catalyst in the lower beds to the upper beds (for example, from Bed 4 to Bed 3; never moving catalyst from Bed 3 to Bed 4). The more highly sulphated lower bed catalyst will always perform very well in the upper beds, but both temperature and chemical effects on the upper bed catalyst prevent it from operating properly in the lower beds.

Caesium-promoted catalyst composition

The caesium-promoted sulphuric acid catalyst is actually very similar to the standard catalyst supplied by MECS. The caesium catalyst is based on a standard potassium-promoted vanadium formulation in which some of the potassium promoter has been replaced with an equimolar amount of caesium (Cs) compounds. The caesium helps to stabilize the vanadium in the molten salt and prevents the precipitation of the vanadium below 410°C as is observed for the conventional sulphuric catalysts. This precipitation results in catalyst deactivation and very low activity at low inlet temperatures. It is important to note that the caesium-promoted catalyst is still a vanadium-containing product just as in the case of the standard sulphuric acid catalysts, thus enabling the caesium catalyst to be handled in a manner identical to the standard sulphuric acid catalysts.

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MECS caesium catalyst products

MECS is proud to offer a wide variety of caesium-promoted catalysts for use in achieving low plant stack emissions and lower ignition temperatures to affect faster plant start-ups.

- XCs-120 (six-lobed, ribbed-ring; all beds)
- Cs-120 (raschig ring; Beds 1 and 2)
- Cs-110 (raschig ring; Beds 2, 3, 4 and 5)
- SCX-2000 ('super-Cs', six-lobed, ribbed-ring; Beds 4 and 5)

Caesium catalyst applications and benefits

The applications and advantages of the caesium catalyst are varied and numerous. The following is a description of some of the applications for this product, which would be of interest to sulphuric acid catalyst customers:

Reduced first bed inlet temperatures

In all first bed installations of the MECS caesium catalyst, the required inlet temperature has been significantly reduced relative to the temperature required for standard catalyst. In some cases, first bed inlet temperatures as low as 360ºC (although optimal performance is around 390°C or greater) have been realized for feed gas containing high SO_2 and high O_2 concentrations. For first bed applications, a 'cap' of the caesium catalyst is loaded on top of the bottom layer of the standard potassium-promoted catalyst (typical recommended caesium catalyst loading is 30-50% of the first bed volume depending upon the operating inlet temperature). The temperature of the gas exiting the caesium catalyst layer is above the ignition temperature of the standard catalyst layer which can then 'complete' the conversion operation within the first bed at a higher level than if a caesium cap were not introduced (Figure 4). It should be noted that once the gas enters the typical ignition temperature zone of standard catalysts (415–420°C), the caesium catalyst provides no additional activity benefit.

Plant restart following short shutdowns

When some sulphuric acid plants must shutdown for short periods, it is often the case that a preheater must be used to reheat the catalyst beds prior to starting up the plant. With caesium catalyst loaded in the first and last pass of the converter, it may be possible to restart the plant without using the preheater, saving both time and fuel costs. Plant start-ups after a cold shutdown are also facilitated by the caesium catalyst in both reduced fuel consumption and short start-up time.

Reduction of SO_2 emissions (double absorption plant)

Through the use of the MECS 'Super' caesium (SCX-2000) catalyst, it is possible to significantly increase the SO_2 conversion through a double absorption plant and hence reduce the SO_2 stack emissions. Stack SO_2 concentrations well below 100 ppm have been realized through the use of the SCX-2000 catalyst in the final beds of double absorption plants (Figure 5). Final bed inlet temperatures within the range of 390–410ºC permit greater conversion due to the shift in the allowable thermodynamic conversion limits. The high conversion levels possible with the caesium catalyst are either unattainable with conventional sulphuric acid catalysts or would require massive volumes of the standard catalyst. There are a number of examples of significant emissions reductions in double absorption sulphur burning, spent acid, and metallurgical plants.

Reduction of SO_2 emissions (single absorption plant)

The use of the MECS caesium catalyst in single absorption plant applications can also significantly reduce the SO_2 concentration in the stack gas. In cases where post-converter scrubbing of the SO_2 is used to minimize emissions, the use of the caesium catalyst can significantly reduce the amount of salts or weak acid produced in the scrubber and save on raw material and waste elimination costs.

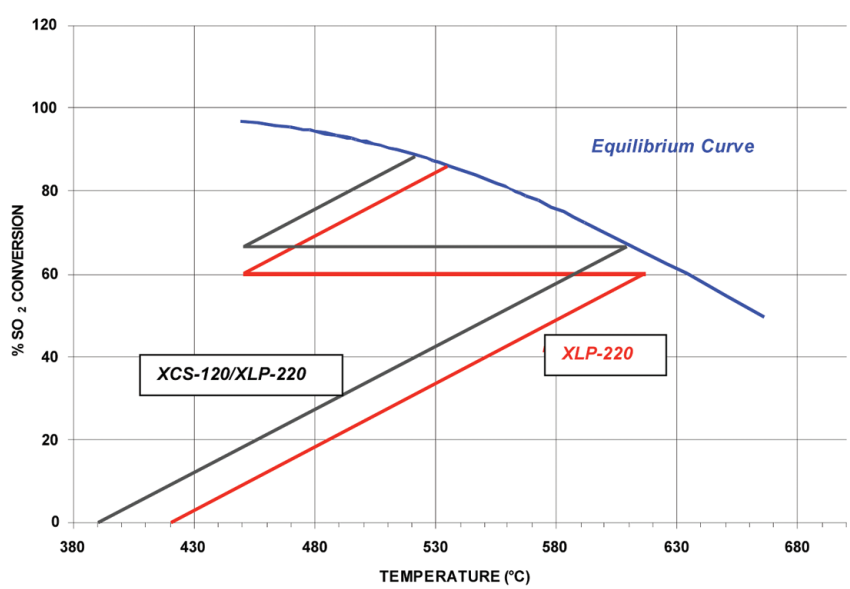


Figure 4—Bed 1 conversion performance with caesium cap

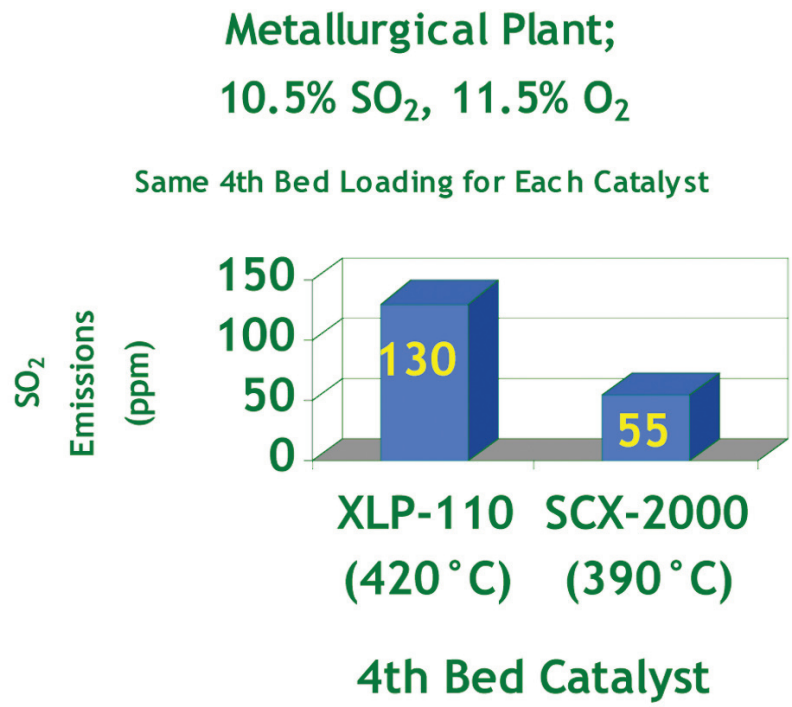


Figure 5—Use of SCX-2000 in a double absorption plant to reduce SO_2 emissions

Control of first bed outlet temperatures

The use of the MECS XCs-120 or Cs-120 caesium-promoted catalysts as a 30-50% 'cap' on the first catalyst bed has been very effective in a number of installations. With this type of application, the caesium catalyst generates sufficient heat (even at low inlet temperatures near 360-380ºC) to 'ignite' the standard catalyst layer below. In this case, the customer takes advantage of the low temperature properties of the caesium catalyst as well as benefiting from the excellent activity of the standard MECS XLP-220 ribbed-rings at the higher temperatures in the bottom layer. An example of this application is found for a large metallurgical plant that has very high SO_2 and O_2 levels in the feed gas. Using conventional XLP-220 ring catalyst in the first pass with a normal inlet temperature of 415–420ºC, the first bed outlet temperature would be in excess of 650ºC, which is unacceptable for long term operations. With a top layer of XCs-120 ribbed-rings, the first pass inlet temperature for this plant can be set at 390ºC with a manageable outlet temperature now less than 640ºC.

MECS technical services

Most catalyst suppliers offer various technical services to support their customers. These services include catalyst sample activity and hardness analyses and some computer simulation studies. MECS extends these services as well as complete world-class sulphuric acid process support. Additionally, for nearly two decades now, MECS has offered the Portable Gas Analysis System (PeGASyS) service for an extensive evaluation of the customer's plant operations. This gas chromatography-based system allows for evaluation the SO_2 and O_2 levels in any accessible gas stream. Uniquely designed gas sampling techniques provide the analytical sample to be free of SO_3 which would damage the equipment. Utilizing this analytical data along with the computer simulation program (SO_2OPT), the operation of the plant can be fully characterized with the results appearing in a detailed report supplied to the customer. There are countless examples of where the PeGASyS service has solved conversion problems, identified heat exchanger leaks, and increased the productivity of sulphuric acid plants; all without having to take the plant down from valuable production.

Summary

This paper has described some of the fundamentals of the standard potassium and caesium-promoted sulphuric acid catalyst formulations along with details of the various factors that can impact catalyst performance. A variety of applications for Caesium Catalyst were presented with the corresponding impacts on performance that can be realized within the sulphuric acid plant. Specific examples were given to assist in quantifying the benefits associated with the use of Caesium Catalyst. Lastly, an update on the MECS technical services extended today for use in characterizing converter performance was also provided.

Acknowledgments

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Also, high praises go to the MECS, Inc. Catalyst Manufacturing Team for its contribution to the production of the high quality catalyst products which include the caesium-promoted catalysts. ◆