

# POISONING OR DEACTIVATION OF MECS<sup>®</sup> CATALYST FOR SULFURIC ACID

## GENERAL

Catalyst life can be shortened significantly when subjected to severe service. Catalyst deterioration may be caused by the following mechanisms:

- **Thermal:** Operation at 650 °C (1200 °F) or higher may cause irreversible degradation of the support.
- **Mechanical:** Dust or scale contacting the catalyst may plug the voids between the rings or pellets and leach the active salts from the catalyst through capillary action.
- **Chemical:** Contaminants react with the catalyst and either reduce activity, cause gradual loss of vanadium or decrease the ring or pellet strength.

Chemical poisons can be grouped according to the type of damage they cause:

<i>Effect</i>	<i>Cause</i>
Loss of Vanadium and Active Salts	Dust, Iron Oxide, Acid Mist, Moisture (below the dew point), Chlorides and Arsenic
Loss of Physical Strength	Fluorides, Moisture and Dust

The following list contains tolerable limits calculated for a 7% SO<sub>2</sub> gas. This can be prorated for other SO<sub>2</sub> concentrations.

<i>Substance</i>	<i>Compound</i>	<i>Approximate Limit (mg/Nm<sup>3</sup>)</i>
Chloride	Cl	1.2
Fluoride	F	0.25
Arsenic	As <sub>2</sub> O <sub>3</sub>	1.2
Lead	Pb	1.2
Mercury	Hg	0.25
Selenium	Se	50
Sulfuric Acid	100 % H <sub>2</sub> SO <sub>4</sub> Mist	50
Dust	--	1.2

Note: Selenium, mercury, lead, cadmium do not generally affect catalyst chemical activity. Their main effect is to the purity and quality of the product acid.

# POISONING OR DEACTIVATION OF MECS<sup>®</sup> CATALYST FOR SULFURIC ACID

## SPECIFIC EFFECTS OF CONTAMINANTS ON SULFURIC ACID CATALYSTS

<i>Contaminant</i>	<i>Effect on Catalyst for Sulfuric Acid</i>
Arsenic (As <sub>2</sub> O <sub>3</sub> , AsH <sub>3</sub> )	At temperatures significantly below 600 °C (1110 °F), the catalyst is saturated with arsenic and a reduced plateau of catalyst activity is reached, which apparently does not change appreciably with further exposure. The decrease of activity appears to be connected with clogging of the catalyst surface by arsenic pentoxide (As <sub>2</sub> O <sub>5</sub> ). At temperatures near 600 °C, the volatile compound V <sub>2</sub> O <sub>3</sub> ·As <sub>2</sub> O <sub>5</sub> can be formed and some long term loss of activity may be noted because of vanadium losses.
Selenium (Se, SeO <sub>3</sub> )	Harmful effect only at temperatures below 400°C (750 °F), initial activity is restored after reheating.
Hydrocarbons (C <sub>n</sub> H <sub>m</sub> )	Harmless in small concentrations. In a few cases, there has been catalyst activity loss as a result of surface deposition of carbon formed by incomplete oxidation of hydrocarbons. The amount of carbon produced is dependent on the properties and concentration of the hydrocarbon, the concentration of oxygen, and the temperature. In high concentrations, heat released from the hydrocarbon oxidation can be a serious problem.
Fluorides (SiF <sub>4</sub> , HF)	Sharply reduces activity, but extremely low levels of F act relatively slowly. HF reacts with the catalyst silica support, forming volatile SiF <sub>4</sub> , and deposition of silica gel on the catalyst surface has been observed.
Iron Sulfate (FeSO <sub>4</sub> )	Mechanically covers the surface of the catalyst and causes loss of activity and pressure drop increase. When catalyst beds contaminated with iron are observed in a cold condition, hard crusts between rings or pellets are noted. The crusts contain appreciable potassium and vanadium as the iron readily reacts with both of these catalyst components. This latter effect leads to catalyst deactivation due to the migration of the potassium and vanadium from the catalyst
Sulfur (S, CS <sub>2</sub> , H <sub>2</sub> S)	Sulfur compounds are not objectionable in small amounts if there is sufficient oxygen to generate oxidation. Large amounts can produce harmful heat releases or block the catalyst surface with sulfur deposits.
Hydrogen (H <sub>2</sub> )	May cause catalyst activity loss by reducing vanadium (+5) to a lower oxidation state. Heat release may also be a problem.
Ammonia (NH <sub>3</sub> )	Harmless in reasonable quantities. Ammonia can be oxidized with objectionable heat release when present in large amounts.
Nitrogen Oxides (NO <sub>x</sub> )	Are not objectionable in low concentrations. (Note that NO may be troublesome in acid plants because it can contaminate product acids and/or cause formation of sub-micron acid mists.)
Water (H <sub>2</sub> O, H <sub>2</sub> SO <sub>4</sub> )	No major effect at temperatures above the typical acid dew points (150-200°C (300-390 °F)). At lower temperatures, there may be degradation of the catalyst with loss of activity and mechanical strength, depending on the extent of condensation. The catalyst can often be regenerated by careful heating. This exposure is the most common mode of catalyst deactivation/breakdown.
Carbon Oxides (CO, CO <sub>2</sub> )	According to various sources, CO specifically does not harm the catalyst. In the presence of large amounts of CO, it is theoretically possible for the SO <sub>2</sub> oxidation reaction to be inhibited due to the reduction of SO <sub>3</sub> via the reaction: (SO <sub>3</sub> + CO → SO <sub>2</sub> + CO <sub>2</sub> ). CO could also theoretically lead to some reduction of the vanadium to lower oxidation states. CO <sub>2</sub> , at any reasonable concentrations, will generally not affect the performance of the sulfuric acid catalyst. High levels of CO <sub>2</sub> in the gas stream will affect the observed temperatures due to its high heat capacity relative to SO <sub>2</sub> /SO <sub>3</sub> /O <sub>2</sub> /N <sub>2</sub> .
Chlorides (Cl <sub>2</sub> , HCl)	These contaminants do not cause significant problems at low concentrations. Extended exposure at high concentrations will lead to vanadium loss through the formation of the volatile compound, VOCl <sub>3</sub> .
Heavy Metals (Pb, Hg)	Although information is limited, analysis results indicate that even small amounts of these contaminants are deposited from the gas phase onto the catalyst surface. This deposition results in significant catalyst activity loss. Where elemental mercury (Hg) is present in small concentrations, its volatility is apparently sufficient to prevent deposition on the catalyst at operating temperatures.

\*Reference: Donovan, J. R., Stolk, R. D., and Unland, M. L., "Oxidation Catalysts for Sulfuric Acid Production": Chapter 7, Applied Industrial Catalysis, Vol. 2 (1983); pp. 271-276.

Copyright © 2014. MECS, Inc. All rights reserved. The DuPont Oval Logo, DuPont™, The Miracles of Science™ and all products denoted with a ® or ™ are trademarks or registered trademarks of E. I. du Pont de Nemours and Company or its affiliates.