

# How shutdown-startup cycles quietly destroy catalyst lifetimes

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Across sulfur burning, metallurgical, spent-acid, and wet-gas sulfuric acid plants, catalyst performance remains central to achieving low SO<sub>2</sub> emissions, regulatory compliance, high production rates, and on-stream time. Plant operators monitor SO<sub>2</sub> emissions and, as the catalyst degrades, adjust converter temperatures to maintain SO<sub>2</sub> emissions within compliance limits. When temperature adjustments no longer work, plant capacity must be reduced. Thermal cycling is one of the operational factors that has a long-term impact on catalyst health and performance. The impact of thermal cycling is persistently underestimated.

Every plant shutdown and restart results in a cooling and heating cycle. These thermal cycles, whether triggered by upstream interruptions, contamination-driven maintenance, or operational choices, exert physical and chemical stresses on the catalyst. These thermal cycles also heat and cool all the metal ducting and equipment in the plant, causing them to expand and contract. These expansions and contractions result in cracking, gas leaks, and more plant shutdowns and thermal cycles. Staying out of this repeated circle of thermal cycles is critical to long-term operation. Specifically for the catalyst, these thermal cycles result in degradation of the catalyst diatomaceous earth support. This degradation leads to increased pressure drop and loss of catalyst activity, which leads to reduced plant capacity, more cold plant shutdowns, and more required catalyst screening and replacement.

This article explains how sulfuric acid catalyst is engineered, how thermal cycling alters it over time, why shutdowns are occurring more frequently in some operating environments, and what practical steps plants can take to extend catalyst life without sacrificing production goals.

## Characteristics of catalyst

Modern sulfuric acid catalysts, such as

the MECS® portfolio, are the product of over a century of development in materials science, pellet geometry, and vanadium chemistry. For 100 years, MECS® catalysts have reliably and economically converted SO<sub>2</sub> to SO<sub>3</sub> across diverse plant types. That longevity reflects continuous innovation around four performance characteristics: activity, pressure drop, hardness, and service life.

At its core, sulfuric acid catalyst uses a vanadium-containing molten salt, supported on a porous diatomaceous earth (DE) or silica-based substrate. This provides:

- High porosity and surface area to expose active sites
- Thermal stability across industrial temperature ranges
- Mechanical strength to resist crushing and dust formation
- Mass transfer efficiency, maintained by keeping open pathways for gas flow

Catalyst stability and durability depend on how the active vanadium salts are dispersed, a selection of DE that optimizes surface area, and how the pellet geometry manages both flow resistance and exposed area. The MECS® family of catalysts are designed for extended campaign duration and resilience, but even the best catalyst formulation and support media have limits when subjected to repeated heating and cooling cycles.

## How thermal cycles affect catalyst

Sulfuric acid catalyst is affected by thermal cycles through three interconnected mechanisms:

1) Breakdown of the support structure through thermal shock:

The diatomaceous earth (DE) or silica-based support is designed for high porosity and thermal stability, but it is not immune to repeated temperature cycles. Each time temperatures rise and fall, the support

expands and contracts. Over enough cycles, this leads to:

- Microcracking and structural fatigue, because the pellet's internal framework is stressed repeatedly.
- Collapse or partial melting of the support at higher temperatures can transform the once porous structure into a dense, amorphous mass.
- Loss of porosity, which means fewer pathways and fewer accessible active sites for SO<sub>2</sub> oxidation.
- Increased pressure drop as the bed begins to compact or generate dust; and lower conversion as the effective surface area declines.

2) Vanadium oxidation state shifts during temperature swings:

For SO<sub>2</sub> oxidation to proceed efficiently, vanadium must remain in its most reactive oxidation states. Thermal cycling disrupts this balance as follows:

- Temperature swings shift the oxidation state distribution, increasing the fraction of less reactive vanadium species. These chemical changes reduce catalytic performance even before any visible physical damage occurs.
- During cooling or dewpoint events with high acid mist or vapor present, the active vanadium-based melt phase can cool and redistribute unevenly, causing localized zones of reduced activity.
- If acid condensate forms, active salts can be leached or washed from the pellet surface, accelerating deactivation.

Thus, even in the absence of structural failure, the catalyst can lose reactivity simply because temperature fluctuations destabilize the chemistry of the active phase.

3) Thermal cycling amplified by contamination:

Thermal cycling rarely acts alone in real operating environments. In many plants, contaminants such as ash, dust, iron oxide, or trace elements are already present in the

gas stream. These contaminants introduce mechanical and chemical stress on the catalyst.

- “99% pure” sulfur contains some solid contaminants. These solids become ash after sulfur combustion and lodge in the catalyst pore structure, increasing pressure drop and stressing the pellet.
- Maintaining an effective gas cleaning system is vital in metallurgical and spent acid plants to remove impurities from process feeds before they can interact with the catalyst, preventing reductions in conversion efficiency or mechanical strength. Even in sulfur burning plants, efficient filtering of the combustion air is critical to catalyst life.
- The need for frequent shutdowns to screen or replace contaminated catalyst introduces additional thermal cycles, which compound the existing degradation issues. The catalyst experiences not only thermal stress but also two simultaneous degradation pathways: thermal cycling and accumulated contaminants.

## Experience from the field

In one observed case, a plant experienced nearly ten shutdowns within a single year. These repeated outages were not the result of poor operational practice within

the acid plant itself, but rather frequent upstream process upsets that repeatedly interrupted the supply of hot process gas. Each interruption forced the catalyst through another temperature cycle. Over time, the cumulative impact severely weakened the catalyst structure, ultimately degrading it into essentially solidified dust, forcing the plant to replace the entire catalyst content prematurely. This anecdote illustrates how dramatically repeated thermal cycles can shorten the lifespan of a catalyst bed.

## Why shutdowns happen more often than they should

Most acid plants are designed and operated with the expectation of long continuous runs; but in many regions and applications, the number of interruptions can be much higher.

Acid plants dependent on metallurgical off-gas or power-related streams face outages when upstream conveyors, furnaces, or boilers are stopped or slowed. When hot SO<sub>2</sub> gas ceases, the catalyst begins to cool unless the plant proactively maintains a high temperature.

High variation of sulfur quality available in the market can also contribute to shutdowns. If sulfur is not effectively fil-

tered, solids will accumulate on the catalyst, increasing pressure drop. Accelerated pressure drop in the catalyst can result in more frequent shutdowns.

Lastly, to reduce downtime, some operations may shorten heat-up times or expose the catalyst to wet heat up gases while it is below the acid dew point. These choices might save hours but could cost months in catalyst life and increase screening losses by amplifying thermal shock and the likelihood of acid dewpoint occurrence.

Each of these drivers increases cycle frequency or severity, which means cumulative damage to the catalyst.

## The cost of ignoring catalyst health

Catalyst is one of the most significant consumables in an acid plant. Not maintaining cycle discipline and exposing the catalyst to repeated thermal cycles will increase catalyst maintenance costs. Even small decisions around sulfur filtration, process gas cleaning or combustion air filtering can have big cost consequences. Let’s look at a short case:

### Material Costs:

With escalating cesium raw material prices, the cost to do maintenance on even a small portion of a cesium bed can reach several hundred thousand dollars. For larger units or multiple beds, costs multiply quickly.

### Indirect Costs:

- Lost catalyst activity, resulting in reduced capacity to meet emissions targets
- Increased catalyst pressure drop, reducing plant capacity and increasing blower power and operating costs
- Increased downtime with associated production loss
- Higher emissions variability during restarts, increasing startup time and reducing plant capacity

These costs can be high when compared with the cost of maintaining temperature during short outages with an external heat source or adhering to disciplined startup procedures. From an OPEX standpoint, avoiding deep or frequent thermal cycles is one of the highest return operational policies available.



Fig. 1: Solidified catalyst bed due to structural degradation.

## Practical strategies to minimize thermal cycling damage

The encouraging reality is that damage from thermal cycling can be minimized. The following operational practices to increase the catalyst life are recommended:

### 1) Maintain temperature during outages:

Minimize heat loss during short outages by minimizing draft through the plant. Consider using an external heat to extend these short outage times when practical. Before cooling below the acid dew point, purge the plant of SO<sub>2</sub> and SO<sub>3</sub>. Field experience shows that keeping beds warm for days is practical and economical compared to premature catalyst replacement. Keep in mind to:

- Purge the plant and then isolate to minimize draft through the plant
- Avoid rapid cooling and reheating

### 2) Follow startup/shutdown procedures rigorously. Follow the manufacturer's procedures and plant standard operating procedures. In particular:

- Heat the catalyst above the acid dew point with dry air before exposing the catalyst to wet combustion gases.
- Observe temperature gradient limits between zones and over time. Note that bed inlet temperatures should not exceed 530°C and temperature differences across division plates should not exceed 140°C.

### 3) Control contaminants at the source:

Every contamination-driven shutdown triggers at least one more thermal cycle. Try to reduce these by:

- Sampling incoming sulfur by lot and include an in-line real-time monitoring system
- Introducing a polishing filter to reduce ash below 8 ppm in sulfur burning plants
- Addressing upstream sources of solids in the sulfur or combustion air
- Using a properly designed and effective gas cleaning system for removing impurities in metallurgical and spent acid plants

### 4) Coordinate with upstream operations:

Where the plant relies on external SO<sub>2</sub> sources, establish clear communication pro-

cedures so supplemental heat can be initiated proactively rather than reactively.

## Monitoring and decision tools

- Temperature trending: Focus on changes in per-pass temperature rise during stable windows.
- Pressure drop surveillance: A pressure increase can be an early sign of dust accumulation from repeated cycles. Investigate promptly. Plant pressure surveys are recommended monthly at a minimum.
- Converter gas sampling and analysis (such as MECS® PeGASyS™ testing): Periodic targeted analyses provide clarity on gas composition changes that can otherwise be mistaken for activity loss. These campaigns are especially useful after several cycling events to inform maintenance planning.
- Shutdown inspections: When outages occur, use the opportunity to inspect for fine accumulation, pellet edge wear, and evidence of moisture or acid mist contact. Collect catalyst samples from each bed for quantitative analysis of activity and hardness.

## Conclusion

Thermal cycling has significant consequences for catalyst degradation in sulfuric acid plants. The engineering behind modern sulfuric acid catalysts is impressive and proven, but cannot fully withstand repeated or poorly managed heating and cooling without accelerated wear.

The good news is that the most effective defenses are operational and practical: maintain temperature during short outages, abide by startup/shutdown procedures, control contaminants at their source, and coordinate closely with upstream operations. Plants that implement these practices consistently experience longer catalyst life, lower emissions, reduced maintenance frequency, and improved economics.

Minimizing thermal cycles and managing them with discipline when they do occur is one of the simplest, highest return strategies for protecting catalyst investments and ensuring reliable, efficient acid production over the long run.

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Fig. 2: A sample of degraded catalyst comprised mostly of dust.