

Sulfuric acid catalyst 101- Revisited with an update

In the Fall/Winter 2002 issue of Sulfuric Acid Today we ran our feature article "Sulfuric Acid Catalyst 101" that covered topics ranging from composition to maintenance. The following revisits this subject matter and includes a review of some catalyst basics with the focus mainly on the issue of pressure drop. We conclude with a current case study on how one producer drastically reduced pressure drop, thereby reducing operating cost and extending run time.

The production of sulfuric acid was revolutionized in the 1920s with the advent of the contact process, which replaced the old lead chamber process. The heart of the contact process was the introduction of a catalyst to convert SO₂ to SO₃. Although many innovations and improvements have been made over the years, vanadium catalyst is still the workhorse of the sulfuric acid industry.

While commonly referred to as vanadium pentoxide catalyst, this is actually a misnomer. There are no oxides present in the catalyst. The vanadium is in the form of complex salt mixtures including potassium or cesium, sulfur and oxygen (alkali vanadium oxy-sulfates). These salt mixtures, supported on the solid silica base, form the catalytically active complex in the catalyst. Potassium and cesium are the promoters in the catalyst.

A unique feature of the vanadium-based sulfuric acid catalysts is that they are formulated differentially, depending on the gas-phase environment. In other words, the composition of the molten salt will be different for catalyst in the first bed compared to the material in the fourth bed.

Pressure drop

The relatively soft catalyst, compared to others in the chemical industry, offers a tremendous surface-to-mass ratio. The trade off is that the harder the catalyst, the lower the activity. However, the softer the catalyst, the more dust is generated. Second to activity, dust is the primary concern in the converter as it directly equates to pressure drop.

Today, catalyst manufacturers strive to find a happy medium where they produce a fairly "dry" catalyst that accommodates the dust, yet has sufficient active ingredients to provide good activity and performance.

The dust capacity is defined as the amount of foreign dust (in weight per

unit bed cross sectional area) that can be accumulated before the pressure drop exceeds a certain level. The dust capacity increases with the void fraction of the bed and the height (or penetration depth) across which the dust is distributed.

The alkali-metal-promoted vanadium catalyst acts as a very effective dust filter due to the fly-paper effect of the pyrosulfate complex that is present as a liquid in the microscopic pores of the catalyst at operating temperatures. Operating temperatures range from 400 degrees Celsius (C) through 630 degrees C or 750 degrees Fahrenheit (F) to 1,165 degrees F.

"Observations from industrial applications have shown that part of the liquid melt migrates from the catalyst into the dust, making it sticky as well. The dust particles pass largely unhindered through the layer of inert rocks or ceramic bodies normally placed on top of the bed. Most of the dust is normally trapped in the upper two to six inches of the catalyst, eventually plugging the gas passage so that screening of the bed becomes necessary to relieve high pressure drop build-up," Sam Chidester, sales manager for Haldor Topsoe in both the United States and Canada, said.

"If you have pressure drop, you want to maintain the dust filters on your plant, prevent and monitor acid carryover from the drying tower or interpass tower - any acid mist carryover will corrode steel duct work and cause iron sulfate, which is a dust that plugs up the catalyst beds and leaches out the catalyst actives. You want to keep the drying and interpass tower in perfect shape with inspections," John Horne, sales director for MECS Inc. added.

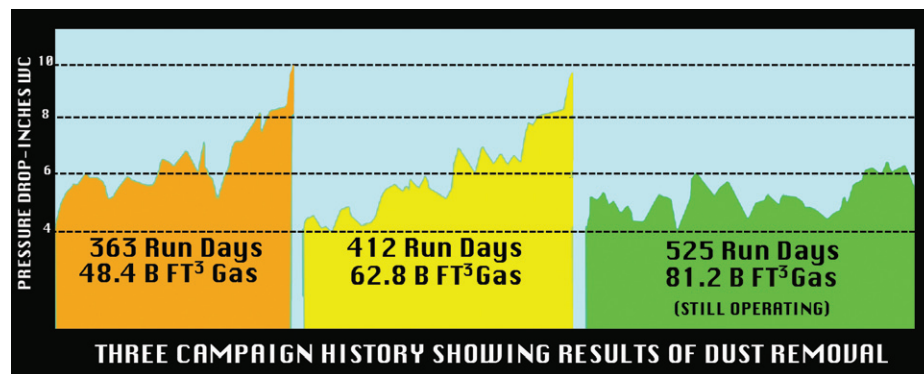
"The first pass is like a filter, and it picks up the dust. Typically, when you get to the second, third and fourth beds of the converter, the beds are fairly clean. You generally do not have to screen these beds as frequently - buildup in these beds is from scale corrosion in the duct work, process equipment and plant upsets," Horne said.

"Screening and contaminants in the process dramatically affect the catalyst. Screening is done to reduce the pressure drop, and in some cases additional catalyst is added for increased conversion. How you screen (the screening rate, and if you use experienced or inexperienced workers) and how you prepare the catalyst for screening will dramatically affect the catalyst's life," according to BASF's Daniel Heineke.

Dust removal should be a comprehensive part of the screening operation rather than just screening for particle size.

Sources of dust in sulfur burning plants include contaminated sulfur, failure of molten-sulfur filters, spalling of combustion chamber brick, equipment or duct scale and vibration of the catalyst itself during operation. Metallurgical acid plants have gas-cleaning facilities, but removal of dust is never 100 percent.

In metallurgical/smelters, regeneration



and sulfur burning plants, there are different types of challenges regarding dust.

"Sulfur burning plants typically do not have a gas cleaning system, so the amount of particulates that wind up in the catalyst is pretty much related to how clean the sulfur is that they burn and the efficiency of their furnace," Chidester said.

"Fertilizer plants tend to have a lot of dust in them from the gypsum stacks and most plants have air filters that filter out a good portion of that dust," Horne said. "Inorganic elements are in the sulfur that do not burn and form an ash. That ash is a major source of dust."

The air that comes in to the plant is dried in the drying tower to exact the moisture from the air. That acid tower typically has a mesh pad or mist eliminators. If the tower is acting up and there is acid carryover from that tower, the acid carryover will corrode with the carbon steel duct work. The corrosion produces iron sulfate, which then blows into the catalyst bed in a dust form. That dust, along with other dust, settles in between the catalyst voids. Toward the end of a run, some two to two-and-a-half years later, the voids can become completely packed with dust causing the pressure drop to get very high.

While the cost of down time and catalyst screening are obvious results of pressure drop, a side effect that often can be even more expensive is energy cost. Steve Purcelli of MECS Inc. noted, "For each inch of reduced water column on the main compressor, there is an annual savings of \$10,000 for a 3,000 stpd acid plant operating with a power cost of \$0.05/kwh" (see formula).

Even if the pressure drop across the catalyst beds is not forcing the plant to shut down it may still be costing hundreds of thousands of dollars per year in additional energy costs to keep the plant running.

One company addressing these issues, VIP International, has recently developed a pneumatic catalyst loading system. The system offers dust-free loading by aspirating the catalyst as it is pneumatically transferred into the converter.

Feryl Masters, process engineer for PCS Phosphate - Aurora, recently utilized VIP's services during a turnaround.

"VIP came in during our May turnaround and loaded our second pass catalyst with their new pneumatic system.

I was highly impressed with how little dust or broken catalyst there was in the bed as they loaded," Masters said.

"The loading this time was totally different from the normal loading - it was much faster, which means it is a lot safer for the workers because the employee exposure is greatly reduced. It's hard to quantify, but it looks like we have a 1-inch to 2-inch W.C. lower pressure drop on start-up than we normally have seen on the second pass," he added.

There are numerous advantages to the pneumatic system. While the primary intent of the system was to give lower pressure drop, the truly amazing loading rate of 10,000 liters to 12,000 liters per hour is an added bonus.

Shane Cornell, production superintendent for sulfuric acid at Mosaic concurred. "I was impressed with the rate of loading - we were able to load over 90,000 liters per shift on our recent outage."

Another consideration when it comes to dust, is employee exposure. With reduced loading time and only two employees in the converter during loading, the new system caught the attention of E.I. DuPont de Nemours & Co.

"Currently, OSHA has occupational safety and health regulatory guidelines for vanadium dust exposure. Vanadium catalyst, which contains vanadium compounds, has a very low exposure limit," Tyrone Chichester, senior engineering associate for DuPont, said. "The threshold limiting value is one measure we use for the measure of the exposure. The ceiling set for vanadium compounds is 0.5 mg/m³ as dust, which is pretty low. We monitor our personnel very closely to ensure they are below the exposure limits."

A new method of replacing the catalyst so that they minimize the amount of dust is an excellent improvement in handling the catalyst because of the reduction of the overall employee exposure," Chichester said.

Catalyst 101 - Update

A metallurgical plant producing 3,000 tons of acid per day was facing severe challenges. After major upgrades and bottlenecking in 2005 the plant was rated for over 141,000 SCFM of gas flow. However, pressure drop issues in the converter limited the plant.

A metallurgical plant is under constant pressure to maintain a 100-percent on-line



factor between planned maintenance outages. As the primary pollution control device for the smelting operation, the sulfuric acid plant's continued operation is mandatory to meet clean air requirements in the production of metal. If the acid plant shuts down, the smelter shuts down. In this case that could mean a loss of production of over \$100,000 per hour.

In 2006 the pressure drop on a particular bed reached 10-inches WC after only 363 days into the campaign and over 30-inches across the entire converter. During this time 48.4 B cubic feet of gas had been processed. After screening, the plant was restarted and ran for 412 days before similar

pressure drops required shutting down for catalyst screening. During this campaign 62.8 B cubic feet of gas were processed. The total amount of gas processed is an important factor and relative to the number of days of run time. At reduced rates, the facility can expect to extend run times.

In an effort to increase run time, the plant turned to VIP International's catalyst handling package including their Pneumatic Loading System. Assured of shorter down time due to the increased loading rates, the producer also hoped for a longer campaign due to the dust removal during the loading. As seen in the graph, the results were better than expected. After 525 days of production

and processing over 81.2 B cubic feet of gas, the converter was still running well with less than 6-inches WC pressure drop across the particular bed and around 23-inches through the entire converter. Production management noted that the pressure spike that precedes the mandatory shutdown had yet to materialize.

This same technology has been utilized in the initial loading of new converters. While catalyst leaves the manufacturer's facility virtually dust free, it may have a long and rough trip to its final destination. VIP's Pneumatic Loading System not only reduces the load time by as much as one third, but also removes the dust generated

during shipment. Actual loading data has shown that 1,000 liters of new catalyst may contain as much as 50 liters of free dust.

In an industry where state-of-the-art is a popular and often sought-after adjective, the catalyst has held its own for the better part of a century. Still, environmental regulations, industry standards and the overwhelming desire for companies to practice safer, greener business have led many catalyst users to seek out enhancements from today's technology. Through the pairing of the best of the old and best of the new – sulfuric acid plants and the producers they process for continue to see dynamic results. □