Catalyst & Technology News

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Reliable Tail Gas Unit Performance Achieved With Proper Monitoring & Response

Claus Tail Gas Units (TGUs) that utilise catalytic reduction and hydrolysis over Criterion 534 or Criterion 234 catalysts will provide optimum overall recovery of sulphur in refineries and gas plants if operated properly. These units are characterized as “Best Available Control Technology” (BACT) because they can recover at least 99.8 – 99.9 percent of the sulphur that enters the Claus plant as hydrogen sulfide feed.

These TGUs can operate stably for very extended periods on a single catalyst charge. However, achieving such stable operation requires tight control of several operating parameters and monitoring of several others to detect potential problems early.

In the Claus reaction, two molecules of hydrogen sulfide react with one molecule of sulphur dioxide to form elemental sulphur and steam. The reaction is simple but, unfortunately, equilibrium controlled. The “tail gas” exiting the Claus Process still contains unconverted hydrogen sulfide and sulphur dioxide, plus carbonyl sulfide and carbon disulfide that arise from hydrocarbon impurities in the Claus feed. The tail gas is fed to a TGU, which uses a specially designed catalyst to help reduce the sulphur dioxide and uncondensed elemental sulphur to hydrogen sulfide and hydrolyze the carbonyl sulfide and carbon disulfide to hydrogen sulfide too. The hydrogen sulfide is then often removed from the mixed gases via an amine system. Regeneration of the amine system frees the hydrogen sulfide so it may be recycled to extinction through the Claus process. In an older variation of the process, the hydrogen sulfide is directly oxidised in the liquid phase to sulphur.

Key Parameters to Control in the Catalytic Process

The three main control parameters are inlet temperature, hydrogen content, and air/fuel ratio in the in-line burner.

Catalyst Bed Inlet Temperature

The inlet temperature is usually held at the lowest temperature that achieves the desired conversions. With active, healthy catalyst, this can be as low as 525°F. Lower reaction temperatures are related to lower equilibrium concentrations of COS and CS_2. However, lower temperatures also lead to slower reactions, so it may be necessary to increase the reaction temperature as the catalyst's activity declines due to its age or operational problems.

Hydrogen Concentration

The hydrogen concentration is usually measured at the quench tower's overhead where temperatures and steam concentrations are lower. The reactor effluent hydrogen concentration may be maintained around one percent with good results. However, it is best to run at higher concentrations (up to three or four percent) to ensure sufficient hydrogen is available to reduce the sulphur dioxide and elemental sulphur during times when minor upsets lead to higher concentrations of these components.

In-line burner Air/Fuel (A/F) ratio

Problems with burner control are the prime cause of premature catalyst failure. When the A/F ratio is above 90 percent, oxygen can bypass the burner and a portion of that oxygen may irreversibly degrade the tail gas catalyst through surface sulfation. At too low an A/F ratio, soot will form from the natural gas fuel. These small particles of soot will plug the pores of the catalyst, reducing its activity. Greater quantities of soot will eventually plug the catalyst bed, shutting down the entire unit due to excessive pressure drop. To ensure optimum A/F ratio control, the fuel and air flow should be pressure and temperature compensated. The A/F ratio should be maintained between 70 and 90 percent.

Key Parameters to Monitor in the Catalytic Process

Incinerator Stack

The key parameter that most operators must monitor and report is the amount of sulphur dioxide being released to the atmosphere. If this quantity stays below the mandated level, no changes to the operation are needed. If the emissions level is below the required level, but climbing, then action must be taken. In this situation, checking changes in other operating parameters may assist in determining what is happening to the catalyst and what action should be taken to delay catalyst replacement.

Quench Water

The quench water should be clear and colorless, and it should have a pH in the range of 6 – 8 without the addition of caustic or ammonia. Sulphur dioxide levels above 10 -ppm will cause the quench water to become milky due to sulphur formation via the "wet Claus" reaction. Sulphur dioxide levels below 10-ppm will not cause the quench water to become cloudy, but trace sulphur dioxide will degrade the amine.

Reaction Exotherm

Most tail gas units are equipped with thermocouples that can be used to monitor the progression of reaction exotherms through the catalyst bed. An unusually high heat rise suggests that the sulphur dioxide concentration in the reactor inlet is very high, or that air is entering the reactor.

The most exothermic reaction that normally occurs in the tail gas reactor is the reduction of sulphur dioxide to hydrogen sulfide. This reaction is also the easiest to catalyze, and usually the last to die. With healthy catalyst, the exotherm occurs predominantly in the first 25 percent of the catalyst bed for almost the entire run period. If operational upsets reduce the catalyst's activity, the exotherm will start to move further into the bed. This indicates that the operating parameters and instrumentation should be reviewed for problems and that a catalyst change out should be planned.

Other catalyst problems can also cause abnormal temperature readings:

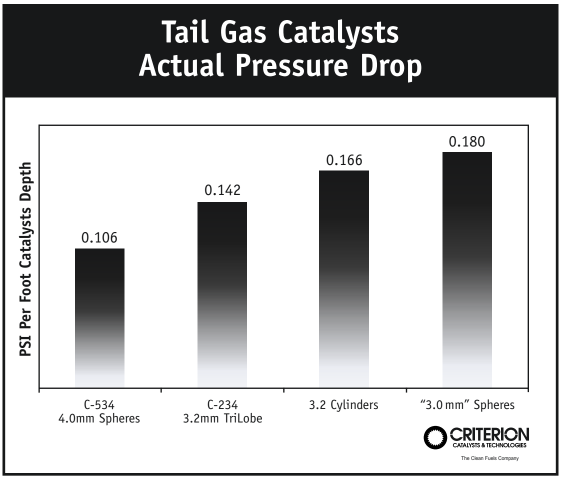
- Catalyst bed displacement
- Catalyst screen leaks
- Wrong thermocouple length / placement
- Damaged flow distributor

Catalyst Pressure Drop

The sulphur plant and tail gas unit operate at atmospheric pressure, with only about five pounds of pressure drop across the entire system including three Claus catalyst beds, the tail gas catalyst bed and all piping, towers and heat exchangers. Any increase in pressure drop across the process carries severe penalties in lost capacity for sulphur handling. In the worst case, crude oil or natural gas must be backed out of the refinery or gas plant, leading to a substantial decrease in the amount of products available for sale.

Catalyst beds are excellent filters. Any source of particulate, such as soot or refractory fines in the tail gas unit can result in pressure drop increase across this catalyst bed. Monitoring the pressure drop continuously to quickly catch rising pressure drop may permit corrective measures to be taken to save the catalyst run. It is a good practice to regularly check the pressure manually with a low range pressure gauge even if the reactor is equipped with a pressure drop instrument. Choosing a tail gas catalyst with low initial pressure drop provides extra margin to cope with bed plugging problems. Criterion's 534 spherical catalyst is the lowest pressure drop catalyst available, followed closely by Criterion's 234 catalyst.

Criterion C-534: Lowest Pressure Drop To Maximise TGU Run Length



Product CO/Hydrogen Ratio

Even at locations where carbon monoxide is not a regulated emission, monitoring CO levels (at constant hydrogen concentrations) can help determine the tail gas catalyst's condition. Usually, the conversion of CO via the water gas shift reaction is one of the first to decline. Thus, an increase in the levels of CO can give advanced warning of declining catalyst activity.

Conclusion

A few relatively simple measurements and observations can provide critical insights into the tail gas catalyst's condition. Fast response to the warning signals can minimize catalyst degradation and extend the time period between shutdowns.

Call your Criterion representative to learn more about improving your TGU operation.

Important:

All information contained in this document is considered accurate at the time of the testing, based on the equipment, and specific conditions and other limitations during the testing process. It is being furnished upon the express condition that the user will make its own assessment to determine the accuracy and applicability for the user's particular purpose.

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