Potential Problems in the Operation of Tail Gas Units

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Abstract

The treating of Claus tail gas to minimize sulfur emissions is required in most places in the world. The reductive tail gas processes where cobalt – molybdenum catalysts are used to reduce SO2, hydrolyze COS and CS2, and shift of CO are considered "Best Available Control Technology" ("BACT"). These catalysts are used in many licensed processes available today. These processes and catalysts permit overall sulfur recoveries of greater than 99.8 percent.

Most of these processes utilize in-line burners to reheat the gas stream and to generate the reducing gas needed for the reactions. Careful operation has resulted in numerous users obtaining useful catalyst lives up to eleven years long. However, to achieve these long lifetimes, a great deal of attention must be devoted to the (a) loading, (b) start up, (c) operation, and (d) shut down of these tail gas treating units. This presentation will attempt to identify the pitfalls related to the operation of the tail gas catalyst.

Introduction

Properly maintained and operated cobalt – molybdenum tail gas catalysts have given satisfactory performance for up to eleven years. These long cycle lengths have their downsides: the personnel that have the experience have transferred, retired, or have been promoted! The change out and start up the catalyst may then fall to staff that are short on actual hands-on experience.

Sulfur plants and tail gas units are quite different from the hydroprocessing plants that populate refineries:

1. They operate at atmospheric pressure!
2. In most cases, they incorporate a burner with air and a real flame!
3. The TGU doesn't really make a product! (…Or money!)

However, an under-performing or non-performing tail gas unit may well result in curtailment of the refinery or gas plant. This WILL result in undesirable upper management attention. Combine all of these factors, and the staff becomes quite nervous about bringing fresh catalyst on-line.

In this presentation, I will attempt to identify the various pitfalls associated with the installation, start up, and operation of a fresh load of tail gas catalyst. The structure I will use is chronological – the order in which one needs to address the various stages of the task. The solutions and observations are offered merely as suggestions for your consideration. YOU are ultimately responsible for the operation of your unit.

Critical Stages in the Life of a Catalyst Charge

Loading

Start Up

Operation

Shut Down

A. Loading

The catalyst beds in reductive tail gas units ("TGU's") are in either a tall, radial flow configuration, or in a thin (three feet thick), flat expansive configuration in order to minimize pressure drop. Since most TGU's are this second type, I will focus my comments on them.

Potential Problem Area: Failure to Use Dense Hold Down Media

TGU catalysts are either spherical, or low density (28 – 38 pounds/ft3). Imperfect gas flow distribution will tend to move the catalyst about unless it is held in place with dense ceramic media. Please see Figure 1. (My personal preference is 0.5-inch spheres, but I do not get to uptight about the size.) Without dense hold-down media, the catalyst can move about within the reactor, making shallow spots where bypassing can occur and reactants pass unconverted. This effect is more likely in large reactors than in smaller ones.

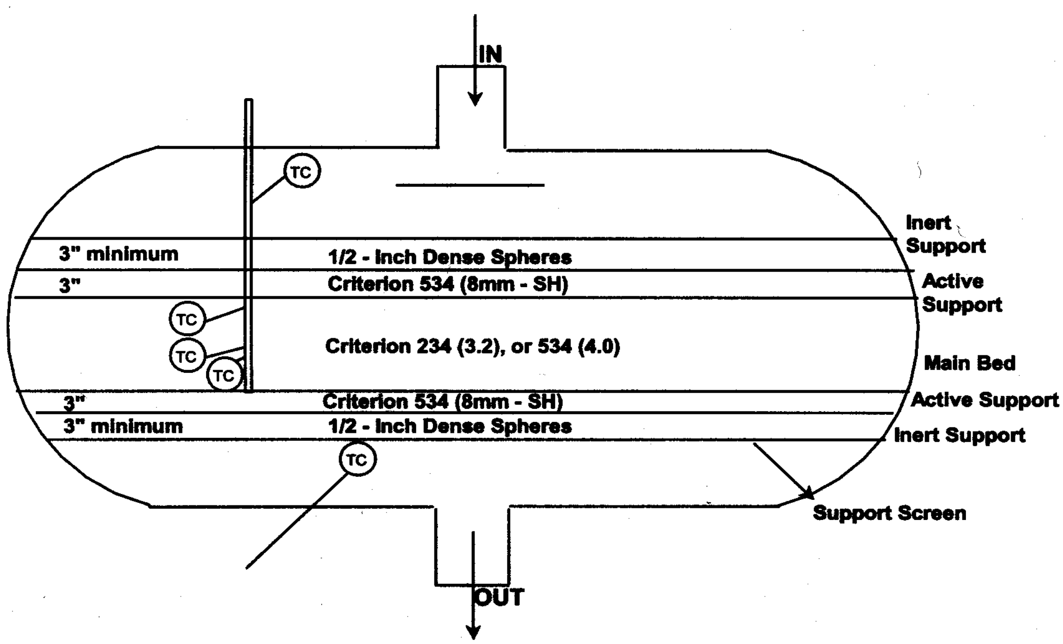

Figure 1

Potential Problem Area: Refractory Dry Out

In new installations, and in equipment where refractory has been repaired, there is the temptation to load catalyst first, and then dry out the refractory. This approach avoids delaying the entire operation to cool down the hardware so personnel can enter the reactor to install catalyst after the dry out. This procedure is acceptable if a few rules are followed:

1. There is the opportunity for dust left over from refractory work to plug the catalyst bed. If the refractory work is undertaken, but not cleaned up properly, the catalyst bed can collect a large quantity of dust. The life of the catalyst charge can then be shortened substantially by pressure drop increases.
2. Catalyst bed temperatures will not exceed 1000 degrees F. The catalyst can be damaged if subjected to extremely high temperatures. Leave the man ways open.
3. The burners must be kept oxidative. Accidental substoichiometric operation of the burners in the absence of a source of sulfur will generate reducing gases that will reduce the oxide form of the catalyst to the metals. The zero valent metals will sinter which results in catalyst with impaired activity.

   $$CoO + MoO_3 + 2\,H_2 \rightarrow Co + Mo + 2\,H_2O$$

   In the worst case scenario, the error is caught, the burner is adjusted to oxidative, and the oxygen reacts with the reduced metals resulting in extremely high temperatures which destroy the catalyst.

B. Start Up and Sulfiding

Entire papers can be written on the details of the sulfiding of fresh catalyst and the start up of presulfurized catalyst. Criterion Catalysts and Technologies, LP offers both fresh and presulfurized catalysts. With careful attention to detail, clients have commissioned numerous charges of these catalysts, both fresh and presulfurized, without any incidents. I will try to hit the high points here.

Potential Problem Area: Hot Air Contacting the Presulfurized Catalyst. The in-line burner must be lit and immediately switched to substoichiometric operation. Failure to do so could possible result in the oxidation of the presulfurizing precursors instead of reduction. In actual practice, we have not had any such problems.

To obtain the desired service from the catalysts, certain operating conditions must be met. Some operational variations from these guidelines will merely result in poor performance. Other operational variations will actually result in destruction of the catalyst.

Sulfiding of Fresh Catalyst: The Criterion guidelines for catalyst sulfiding and catalyst loading must be followed in order to obtain maximum activity from the tail gas catalysts. The Sulfiding method we recommend is given in our website, www.criterioncatalysts.com. To understand the requirements of sulfiding that will result in optimum activity, one needs to understand the chemistry that is occurring. The fresh catalysts are comprised of cobalt and molybdenum oxides, CoO and MoO_3. The active catalysts are comprised of the sulfides of these metals, CoS and MoS_2. The conversion of the cobalt is relatively straightforward:

$$CoO + H_2S \rightarrow CoS + H_2O$$

However, the conversion of the molybdenum is more complicated because the molybdenum changes oxidation number from six to four. This requires a reducing agent, and hydrogen sulfide itself appears unable to do it by itself. Hydrogen is required. The level of hydrogen generated by in-line substoichiometric burners is quite adequate.

$$MoO_3 + 3H_2S + H2 \rightarrow MoS_2 + 4H_2O$$

These reactions are exothermic, so care must be taken to sulfide at a rate that localized overheating does not occur. At the same time, temperatures of at least 600 ^{o}F (315 ^{o}C) are required to complete the conversion.

Sulfur dioxide will impair the proper sulfiding reactions. If Claus tail gas is used for sulfiding, the ratio of H_2S to SO_2 in the tail gas should be increased to 7:1 or higher.

Potential Problem: Insufficient Hydrogen During Sulfiding.
The conversion of the molybdenum oxide to the molybdenum sulfide is not complete unless reducing gas is present. If the molybdenum is not completely converted, the activity of the catalyst will be impaired. This problem may be corrected "on the fly" by merely switching the normal operation to a high H_2S / SO_2 ratio and increasing the temperature.

Potential Problem: Inadequate Temperature to Complete the Sulfiding.
In some cases, operational problems have caused an interruption in the sulfiding without the proper temperature being reached. This also can be corrected "on the fly" by merely switching to a high H_2S / SO_2 ratio in the presence of excess hydrogen, and increasing the temperature to the proper level.

C. Operation

The function of the TGU catalyst is to convert all sulfur – containing compounds to hydrogen sulfide and carbon monoxide to hydrogen via the water-gas shift reaction. The conversions of carbonyl sulfide, carbon disulfide, and carbon monoxide are limited by equilibrium. Sulfur dioxide reduction, the most exothermic of the reactions, will go essentially to completion. Typical feed and product compositions are shown in Figure 2. The reactions by which these components interact are shown in Figure 3.

TYPICAL GAS COMPOSITION IN TAIL GAS TREATING PROCESSES (Figure 2)

COMPONENT	RX FEED, 2	RX OUTLET, 3
H_2S	0.79	1.74
SO_2	0.39	
S_8	0.05	
CS_2	0.05	
COS	0.09	
CO	0.32	
CO_2	2.98	3.46
CH_4	0.03	0.03
H_2	1.99	0.78
H_2O	32.25	32.66
N_2	61.06	61.33

TYPICAL REACTIONS IN TAILGAS TREATING REACTORS (Figure 3)

Metal Catalyzed:

$S_2 + 2H_2$ -------------------> $2H_2S$

$SO_2 + 3H_2$ -----------------> $H_2S + 2H_2O$

$CO + H_2O$ -------------------> $CO_2 + H_2$

Surface Area Catalyzed:

$COS + H_2O$ ----------------> $CO_2 + H_2S$

$CS_2 + 2H_2O$ ---------------> $CO_2 + 2H_2S$

Undesirable Side Reactions:

$SO_2 + 3CO$ ----------------> $COS + 2CO_2$

$S_2 + 2CO$ ------------------> $2COS$

$H_2S + CO$ ------------------> COS

Mis-Operation Which Will Result in Unsatisfactory Performance

Potential Problem: Insufficient Hydrogen Content. The gas stream passing over the catalyst must contain a slight excess of hydrogen over the hydrogen required to reduce the SO2 and sulfur vapor that is present. If essentially all of the hydrogen is consumed, and SO2 and/or sulfur vapor remain unconverted, then these components will pass into the quench system and the amine system. Fouling of the quench system and destruction of the amine will occur.

A sudden drop in acid gas to the Claus plant can cause a spike in SO2 entering the tail gas unit, and a temperature spike will occur. If the hydrogen is exhausted, a temperature spike will still occur, but some of the SO2 will pass into the quench and amine systems, and will foul these systems.

Potential Problem: Hydrogen Purity. Some tail gas units are constructed to take advantage of supplemental refinery hydrogen. If this hydrogen contains higher hydrocarbons, then sooting of the catalyst bed can occur. In the worse cases, pressure drop will require a shutdown of the unit. The catalyst can usually be saved by inert entry – inert screening – inert reload. *Ex situ* regeneration may be required. *In situ* regenerations are difficult to control, and therefore are not recommended.

Potential Problem: Catalyst Bed Temperature. The catalyst performs well in the range of inlet temperatures from 270 to 300 deg C. The lowest temperature that achieves the air quality goals should be utilized to take advantage of:

- Minimizing hydrothermal aging of the catalyst
- Minimizing COS, CS2 and CO in the outlet gases by taking advantage of the equilibrium benefits at the lower temperature.

If reactions become sluggish as the catalyst ages, then higher temperatures can be used to increase reaction kinetics.

Potential Problem: Sulfur Content. If a Claus sulfur condenser drain becomes plugged, then excessive sulfur can enter the tail gas unit and consume all of the available hydrogen. Fouling of the quench system will then occur. Under-deposit corrosion can radically shorten the life of the quench tower.

Mis-Operation Which Will Destroy Catalysts

Destruction of the catalyst is almost always related to the introduction of oxygen into the hot, sulfided, catalyst bed. Large slugs of air will result in huge exotherms (up to 1100 ^{o}C (2000 ^{o}F or more) and conversion of the catalyst to gray dust. Low levels of oxygen can arise from:

- Poor mixing in the burner.
- Operation of the burner at an air/fuel ratio that is above ninety percent of stoichiometry.

These low levels of oxygen will result in surface sulfation of the catalyst which is more difficult to detect, but can insidiously degrade the activity of the catalyst over time.

D. Testing Catalyst for Impaired Activity

It is valuable to be able to monitor the operation of the tail gas catalyst on-line in order to make operational changes as necessary and to be able to anticipate the need for changing the catalyst before the need becomes critical. On-line, one can best keep track of the health of the catalyst charge by watching for trends in the following parameters:

- Quench water pH and clarity
- Catalyst bed delta temperature
- Sulfur dioxide in the incinerator stack
- Carbon Monoxide/Hydrogen Ratio

If it is possible to obtain a representative sample of the catalyst without the sample being oxidized, then physical, chemical and visual tests can be run. These tests include:

- Appearance
- Crush Strength
- Surface Area
- Surface Sulfate/Sulfide Ratio
- Activity

E. Shut Down

Tail gas catalysts may last for a long time, but eventually they must be replaced. These sulfided catalysts are inherently pyrophoric. Also, in use, the catalyst beds filter out iron sulfides that result from upstream corrosion. These iron sulfides will cause the catalyst to ignite upon exposure to air.

There are only two viable alternatives for handling the spent tail gas catalyst, passivation and inert removal. (I do not consider oxidation a "viable" alternative – see "Mis-Operation Which Will Destroy Catalysts" section above.) Passivation is tedious and time consuming. When catalyst reloading is "critical path" to the entire operation, I strongly suggest inert entry and vacuum removal of the catalyst using specialized catalyst handling firms. Catalyst stabilization can then be undertaken safely off-site.

Conclusion

With reasonable attention to detail, the reductive tail gas unit may be operated for extended periods to correspond with any reasonable turn around cycle.

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