

Sulfiding of Tail Gas Catalyst

Proper Preparation of Tail Gas Hydrogenation Catalyst for Long and Active Life

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Abstract

Reductive tail gas catalyst processes such as the SCOT®, Result®, Beavon®, etc., allow sulfur producing facilities such as refineries and gas plants to meet stringent sulfur emission regulations. These processes include reactors containing cobalt-molybdenum catalysts. It is critical that the proper methods are used to convert the as-manufactured tail gas catalyst to the active sulfide form so the tail gas process will operate up to its potential.

This paper addresses the proper loading and *in-situ* sulfiding of the as-received tail gas catalysts for use, the various approaches that can be used depending on variations in the equipment included in the construction of the tail gas unit and the proper care of sulfided catalyst.

Disclaimer

The procedures that are described in this paper are general in nature due to the large variations in SCOT and tail gas units. The user of tail gas catalysts should confirm the applicability of these procedures with the supplier of the catalyst.

Introduction

The Claus Process

Large quantities of hydrogen sulfide, H₂S, are generated when crude oil fractions are hydrotreated to reduce the level of contained sulfur. Much of the natural gas that is produced also contains hydrogen sulfide that must be removed. Sulfur compounds are also released when metals are smelted from sulfur-containing ores. Hydrogen sulfide is an extremely toxic, foul-smelling gaseous compound that must be captured.

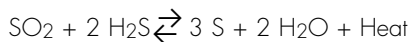
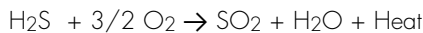
The Claus process is used almost exclusively to convert larger quantities of hydrogen sulfide to elemental sulfur. Elemental sulfur is stable and essentially non-hazardous. It is used to manufacture sulfuric acid and as a component of fertilizer.

*Brimstone Sulfur Recovery Symposium
Vail, Colorado
September 11-14, 2007*

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In the Claus process, as it is currently used, a concentrated stream of hydrogen sulfide is partially burned to form sulfur dioxide. The sulfur dioxide then reacts, first thermally, and then in subsequent steps, catalytically, with hydrogen sulfide to form elemental sulfur. The produced sulfur is easily transported as a melt or as a solid.



This reaction to form sulfur is in equilibrium, so conversion to sulfur is increased by condensing the product sulfur, reheating the mixture, and taking subsequent steps to lower reaction temperatures. The recovery essentially stops when the temperature of the reaction is so cool that the product sulfur condenses in the catalyst. With this limitation, higher temperatures limit sulfur recovery by shifting the equilibrium towards the reactants. Increased pressure in the Claus process requires higher reaction temperatures. The increased temperatures also then limit sulfur recovery via this process.

Large volumes of nitrogen from the air used in the combustion of the hydrogen sulfide and the large volumes of produced steam exit the process. Unfortunately, unreacted sulfur dioxide, unreacted hydrogen sulfide, and uncondensed elemental sulfur are also contained in this stream.

The Claus process chemistry is further complicated in that carbon-containing compounds that enter the process (CO, CO₂, hydrocarbons) react to form carbonyl sulfide, COS, and carbon disulfide, CS₂. These compounds participate in even more complex equilibria. This mixture of dilute compounds in the steam and nitrogen stream is labeled "tail gas." The sulfur species included in the tail gas comprises two to five percent of the total sulfur entering the Claus process. For many years, Claus process operators were allowed to merely incinerate this complex mixture to sulfur dioxide, a less toxic, less odoriferous compound, and release it to the atmosphere. Under this scenario, the recovered sulfur comprised only about 94-97 percent of the sulfur entering the process. The balance of the sulfur, 3-6 percent, polluted the environment as SO₂.

Tail Gas Processes

Various tail gas units (TGU) were developed to increase the recovery of sulfur and address this pollution problem. The best performing (in their ability to recover sulfur) of these are the type that utilize cobalt-molybdenum ("Co-Mo") catalysts. These catalysts allow the sulfur

species in the tail gas to be converted to hydrogen sulfide via reduction with hydrogen and hydrolysis by the steam. Reactor inlet temperatures of about 200-300 °C (390-570 °F) are utilized. The hydrogen sulfide that is produced is then captured in a downstream amine system and returned to the Claus plant for recycling.

The reductive type tail gas units, as represented by those offered by Shell Global Solutions (SCOT), British Gas/Unocal (Beavon), Bechtel, Fluor, TPA, etc., incorporate cobalt-molybdenum on alumina catalysts to reduce the SO₂ to H₂S, and to hydrolyze COS and CS₂ to H₂S so the H₂S may be either absorbed in a circulating amine solution or directly oxidized to sulfur. These processes, when properly operated, convert nearly all of the sulfur species (SO₂, COS, CS₂, elemental S) to H₂S. The H₂S is captured which permits the recovery of 99.8 percent or more of the sulfur fed to the Claus unit. Less than 0.2 percent of the sulfur escapes.

Loading and Sulfiding of the TGU Catalyst

The Co-Mo catalyst that is used in the TGU is manufactured and loaded into the tail gas unit reactor with the catalyst metals in an oxide form. The catalyst is not active until its metals have been converted to sulfide form. Routinely, the catalyst is converted from the oxide form to the sulfide form using the hydrogen sulfide that is readily available either as Claus feed or Claus tail gas.

In some cases, due to strict regulations or convenience, the catalyst is loaded with a presulfurizing agent already coated on it. In an atmosphere of hydrogen and with gentle heating, hydrogen sulfide is generated that converts the active metals to the active sulfides. Terry McHugh of Porocel and I discussed this option in a paper presented last year.

Preparation of Equipment During Turnaround

When the equipment is empty, cold and safe is the best time to check to be sure that the equipment will perform during sulfiding and operation. Inspections should include, but are not necessarily limited to the following:

1. Acid gas bypass line – is it clear of solid sulfur? Do the valves open and close, and are they clear of solid sulfur? Is the line equipped with a nitrogen purge so it can be cleared and kept clear after use?
2. Recycle blower line – is it also clear of solid sulfur? Again, do the valves open and close and are they clear of solid sulfur? Does the blower work? Is the impeller in good condition? Is the line equipped with a nitrogen purge so it can be cleared and kept clear after use?

3. Do the thermocouples sense at the proper level in the catalyst bed?
4. Do the burner controls for the air and fuel work properly? Do the valves respond properly?
5. All refractory should be inspected.

Catalyst Loading

For the tail gas catalyst to operate properly, it must be loaded into the reactor so it will not blind the screen on which it is placed and so it will stay in place. To maintain pressure drop at a minimum, the most common reactor configuration is with a flat bed that is three to five feet deep.

Gas flow rates through the tail gas reactor are extremely high, and pressure drop must be kept to a minimum so the Claus process in front will not back up. Usually the flow diffusers in tail gas reactors are less than ideal, and flow of the gas process stream is mal-distributed across the catalyst. Under these conditions, especially in larger reactors, relatively dense spherical catalyst and less-dense extruded catalyst will move about creating thin areas that allow bypassing of the catalyst and incomplete conversion. This movement will also attrit the catalyst to fines that will increase the pressure drop in the catalyst bed. To keep the catalyst particles from moving, the catalyst should be held in place with dense spherical ceramics. In addition, to help keep the relatively small catalyst particles from blinding the screen on which they are placed, the screen should be first covered with a layer of spherical ceramics.

A favored approach is to use 13 mm dense ceramic spheres at the very bottom of the catalyst bed, on the screen, and at the very top, to hold the catalyst in place during operation. Therefore, at a minimum, the bottom screen must be coated with a 3-6 inch (8-16 cm) of larger ceramic spheres. I prefer 13 mm diameter spheres in this service.

It is common to minimize pressure drop at the interface between particles of different size by keeping the particle size differences of the interfacing layers down to 50%. The user then has the option of grading the bed to minimize pressure drop by utilizing an intermediate sized material, either "active support," Criterion 534 8 mm spherical cobalt – molybdenum catalyst, or dense ceramic spheres of an intermediate 8 mm size. The final, preferred "parfait" of materials in the reactor then are, from bottom to top, 13 mm dense ceramics, 8 mm active support catalyst or dense ceramics, the main catalyst bed, the 8 mm intermediate active catalyst or ceramics, and finally, the 13 mm dense ceramics on top.

Instruments and Capability

Before sulfiding the catalyst, the unit should have an operating hydrogen analyzer and manual gas sampling tubes in a variety of ranges from 1% down to 100 ppm. The equipment should be aligned with an operating incinerator. Source of hydrogen and hydrogen sulfide should be guaranteed so when the catalyst bed is warmed, these reactants will be available when needed.

NOTE: *All sampling of streams that have the potential of containing hydrogen sulfide should be done in accordance with the site's HS&E regulations. This may include full SCBA suits and with backup.*

Catalyst Sulfiding

The steps that are required to actually sulfide the catalyst are dictated by:

1. The equipment available on the tail gas unit.
2. The cognizant emission regulations. (In some locations, a variance to the regulations is allowed for turnaround activities, in other areas it is not allowed.)

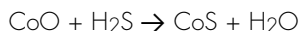
Many of the newer tail gas units are equipped with a Claus feed gas bypass system that provides high concentrations of H₂S to the heater/reactor system and also have a recycle gas flow with either a blower or a steam eductor. The other type of tail gas units are those that do not have access to acid gas (Claus feed gas) and do not have a gas recycle system. The procedure necessary to sulfide the catalyst is different for these two groups of units. For those operators of tail gas units with recycle systems, it is important that they also be aware of the other procedure. In case of equipment failure, it may then be necessary to change procedures so the sulfiding may be completed.

More often than not, when the sulfiding procedure is started but no reactants have yet been added, the catalyst bed shows an exotherm for no apparent reason. It should be remembered that the tail gas catalysts are supported on various high surface area aluminas. These aluminas are desiccants. The catalyst absorbs any moisture in the system and gives off heat. The moisture arises from the combustion of the natural gas in the reducing gas generator burner, the combustion of natural gas in the heat up of the Claus catalyst beds, and from residual moisture in the circulating system such as the quench tower. Otherwise, this moisture is of little consequence because the open, wide pores of the catalyst allow it to freely release the moisture without the "popcorn" steam explosions that can break up other catalysts and cause a pressure drop increase due to the creation of catalyst fines.

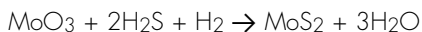
Chemistry of Sulfiding

The active form of the catalyst is the intimate mixture of the cobalt sulfide and molybdenum sulfide. The atmosphere must be low in oxygen, less than 0.5%, for the proper sulfiding to occur.

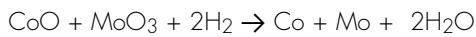
Cobalt oxide is sulfided in a simple one-for-one exchange of the sulfur from the hydrogen sulfide to the oxide that leaves as water.



The sulfiding of the molybdenum oxide is more complex. The molybdenum must be reduced from the Mo (VI) oxide to the Mo (IV) sulfide. To accomplish this reduction, hydrogen is required.



Caution must be exercised to keep the catalyst from being exposed to hydrogen in the absence of hydrogen sulfide above 200 °C (390 °F). If this happens, the active metals on the catalyst will be reduced to the metallic state.



In the metallic state, the metals will sinter into larger clusters. Once sulfided, the catalyst will have impaired activity.

An Important Note on Hydrogen Purity

Hydrogen is required for the sulfiding of the tail gas catalyst, and for the tail gas reduction reactions. Hydrogen is added to indirect-heated systems and to some processes heated by Reducing Gas Generator (RGG) burners. This hydrogen must be free of higher hydrocarbons, like those above propane. Hydrogen containing these higher hydrocarbons is acceptable for hydrotreaters, but tail gas units operate at very low hydrogen partial pressures. At these conditions, the higher hydrocarbons, especially BTEX contained in naphtha reformer hydrogen, will coke on the catalyst, impairing the catalyst's activity and adding to pressure drop. Depending on the level of these impurities, the tail gas unit catalyst may become inoperable in less than two weeks.

The sulfiding reactions are exothermic. The catalyst itself can, within limits, take exotherms in stride. The hardware may not survive extreme exotherms and fail. Therefore it is preferred to keep the exotherm, the difference between the inlet and bed maximum temperature, to less than 30 °C (50 °F). In sulfiding, it is necessary to keep MASS FLOW in mind. The flowing gas moderates the exotherm of the reactions.

Sulfiding of Catalyst in Tail Gas Units with Recycle Systems and Acid Gas Bypass

Recycle systems in tail gas units have a circuit driven by either a blower or a steam eductor. The recycle is usually drawn downstream of the quench and returned upstream of the heater. Normally, these systems have a source of concentrated hydrogen sulfide from either Claus feed or the amine regenerator of a nearby tail gas unit. With this arrangement, it is possible to fully sulfide a tail gas catalyst so that the tail gas unit is ready to operate before the Claus unit is started up. With the use of a sulfur dioxide-free hydrogen sulfide source, it is possible to commission the quench tower (with the capability of pH adjustment) and the amine system. With these in use it is possible to essentially capture all hydrogen sulfide associated with the sulfiding without any escape to the atmosphere via the incinerator. If the entire amine system is started lean, and care is taken to add only the necessary excess hydrogen sulfide, the amine system will hold almost all of the extra hydrogen sulfide without commissioning the regenerator, if that is necessary.

The sulfiding procedure is started by freeing the system of oxygen down to less than 0.5%. This is usually done by purging the system with nitrogen, but can be done by operating the RGG burner at sub-stoichiometric conditions.

The sulfiding should be started before the bed temperature reaches 200 °C (390 °F) to avoid the chance of reducing the catalyst or starting out with too robust an exotherm. If a RGG burner is used for heat, hydrogen will be in the stream. Hydrogen should be adjusted in the 3-5% range. Hydrogen sulfide should be added as the highest bed temperature reaches this temperature. The catalyst should be warmed at a temperature that does not exceed 30 °C (50 °F) per hour.

With the efficiencies of recycle, the hydrogen sulfide levels may not increase appreciably and the exotherm may be modest. This apparent lack of result is due to the rapid uptake of the hydrogen sulfide and the efficient removal of the heat of reaction. The operator may wish to hold at this temperature until the exotherm is apparent to ensure that hydrogen sulfide is really entering the reactor. Hydrogen sulfide analyses of the reactor inlet using low range sample tubes may be necessary.

Once the sulfiding is confirmed, the temperature may be increased. The temperature should be increased to a maximum of at least 315 °C (600 °F) or to the maximum of the capability of the heating system. This temperature should be held for about four hours after all of the bed temperatures reach this level and the inlet and outlet hydrogen sulfide concentrations are equal, and at or above 1.0%.

As the sulfiding is proceeding, a step that may require about 16 hours, the procession of exotherms will be seen proceeding through the catalyst bed. The exotherm will first be seen in the top of the bed, and the temperature in each level will peak above the inlet temperature, and then decrease to the inlet temperature. After the hold period, all exotherms will have subsided, and the inlet and outlet H₂S concentrations will be the same.

The reactor inlet temperature may then be decreased to the preferred level and Claus tail gas may be introduced. If the Claus process is not ready, the tail gas process may be held on standby. At these modest temperatures, pressures, and hydrogen concentrations, it is difficult to strip the catalyst.

Care needs to be taken in bringing the Claus process on line. During the warming of the Claus reactors with natural gas, the burners need to be either operated at less than 90 percent of stoichiometry or bypassed around the sulfided tail gas catalyst. Otherwise, the oxygen in the gas exiting the Claus process may well destroy the sulfided tail gas catalyst, or impair its activity with a large exotherm arising from oxidative reactions.

Sulfiding of Catalyst in Tail Gas Units Using Claus Plant Tail Gas

This procedure is also applicable to tail gas units that incorporate recycle blower systems but use tail gas as the source of the sulfiding gas. This procedure may be considered when there is a failure in the acid gas bypass or recycle blower systems. These failures may take the form of plugged acid gas lines, plugged bypass lines, jammed valves, broken blowers, or broken steameductors.

Claus process tail gas, to be useful for sulfiding, must be rich in hydrogen sulfide in comparison to sulfur dioxide. Whereas the stoichiometric ratio is 2:1 H₂S : SO₂, and some operators prefer to maintain a ratio of 4:1, the ratio should be moved to at least 7:1 or higher to be useful for catalyst sulfiding. Even so, the tail gas still contains sulfur dioxide so it should not be run into the amine system unless the quench system is used as a scrubber. Otherwise, a portion of the amine will be converted to heat stable salts.

Claus tail gas also contains carbonyl sulfide and carbon disulfide which are not useful for sulfiding but do contribute to sulfur dioxide emissions when vented through the incinerator. Elemental sulfur in the tail gas can condense in the catalyst if introduced when the tail gas catalyst is too cool. As the sulfiding procedure is continued, the sulfur will vaporize out of the catalyst, and as the catalyst becomes active, the elemental sulfur will be converted to hydrogen sulfide.

In some cases, the components of older sulfur plants and tail gas units are "hard piped" so there are no bypass valves. In this case, the procedures are straightforward, the only options being to drain the quench tower and amine absorber or direct oxidizer contactor prior to initiating the sulfiding procedure.

The problem with a tail gas unit without a recycle system is the shortage of mass flow during the sulfiding process. Without mass flow, the exotherms can be sharp and difficult to control. The flue gas from the RGG burner provides minimal mass. Nitrogen can be added, but it is expensive and usually in short supply. Steam can be added once the entire tail gas catalyst bed is operating above the capillary dew point of water. One way of gaining mass flow is to couple the necessary heat up of the Claus catalyst beds with natural gas firing with the heat up and sulfiding of the tail gas catalyst. If the Claus burner can be safely operated at 90 percent of stoichiometry to minimize oxygen (and avoid sooting the Claus beds), then the produced flue gas is useful for adding mass flow to the tail gas reactor.

If possible, the Claus plant should be operated at a maximum of about 40 percent of design capacity. The Claus plant ratio should be maintained as stated, above 7:1 ratio, and the RGG burner should be operated at substoichiometric ratio to generate hydrogen. Due to the lack of mass flow, catalyst bed temperatures may be difficult to maintain. The heating of the beds needs to be timed so as to not exceed the temperature limits before hydrogen sulfide is available. Sometimes the flexibility of the start of the sulfiding process is limited by the turndown capabilities of the RGG burner. In these cases, the start of sulfiding is a moving target.

At this point in the sulfiding procedure, the temperatures and rate of temperature increases follow those presented in the previous section on sulfiding with systems with recycle. However, the end of the sulfiding procedure using tail gas is merely switching the Claus plant to the desired H₂S : SO₂ ratio and decreasing the reactor inlet temperature to the desired level.

An Important Note on Reaction Exotherms

As the tail gas unit is operating normally, the primary source of the exotherm in the catalyst bed is the reduction of sulfur dioxide in the tail gas. If the Claus is operating normally, the concentration of SO₂ will not vary widely. Therefore, the exotherm will not vary either, and will remain in the 20-40 °C (35-70 °F) range. Abnormally high exotherms suggest that air is entering the reactor. These sources of air must be corrected or the activity of the catalyst may be seriously impaired.

Conclusion

The tail gas unit with RGG burner is different from about any other process in the refinery. A fuel is burned in air in the process, not in a separate step as in catalyst regenerators. This, plus the fact that the normal life cycle on a tail gas unit catalyst batch may exceed the tenure of the engineers on the staff, does lead to some apprehension. However, attention to HS&E procedures, attention to detail, and a well-documented plan will result in the process being available on time to keep the facility in environmental compliance.

Acknowledgements

The author wishes to thank the following individuals for their valuable assistance:

Lon Stern, Consultant
Mike Huffmaster, Consultant
Patrick McGillicuddy, Shell Global Solutions
Charles E. Wilson, Shell Global Solutions
Kevin Robertson, Shell Oil Company

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