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EASIER STARTUPS IMPROVE SULFUR PLANT RELIABILITY

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Sulfur recovery plant reliability is crucial to the economic success of today's petroleum refineries and gas processing plants. National and regional emission standards simply will not allow these refining and processing facilities to operate for any significant period without their sulfur recovery plants operating at or above the required recovery efficiency. Ortloff has maintained a constant effort since the late 1960s to develop design concepts for sulfur recovery, tailgas cleanup, and tailgas incineration units that improve the reliability and operability of these often-troublesome process units.[1] This article discusses one of the Ortloff sulfur plant design concepts that differs from accepted "industry practice" – cold reactor bed startup.

Cold Reactor Bed Startup Theory

Most sulfur plant designers and operators accept that the catalyst beds in a sulfur recovery unit (SRU) must be above 300°F (150°C) before introducing acid gas into the SRU to avoid plugging the reactors with sulfur. In conventional SRU designs, the reactor beds are heated by firing the acid gas burner with fuel gas and allowing the fuel gas combustion products to flow through the catalyst beds and heat them. If the catalyst in the reactors is not new, it will contain a significant amount of elemental sulfur in its pores from previous operations, even if a "sulfur strip" was performed on the reactors when the SRU was shut down. If free oxygen is present in the combustion products and comes in contact with the catalyst, this residual sulfur will begin to oxidize and cause sulfation of the catalyst. If sufficient oxygen is available, the extreme temperatures created as the sulfur burns on the catalyst can damage the catalyst and the reactor vessels.

In order to minimize the amount of oxygen reaching the catalyst beds, most operating procedures require that the fuel gas combustion be controlled very close to stoichiometric air, so that the combustion products contain little or no oxygen. This mandates very close operator attention during the warmup procedure to keep the air:fuel gas ratio from being too high (which would allow free oxygen to reach the catalyst) or too low (which would cause the burner to form soot and foul the catalyst with carbon). Also, if the reaction furnace is not already up to operating temperature, the operators must inject quench steam or inert gas to keep the temperatures in the furnace low enough to prevent damaging the furnace refractory by heating it too rapidly.

Ortloff concluded that these problems (catalyst sulfation, heat damage, furnace overheating) could all be eliminated if the catalyst beds were not warmed up prior to introducing acid gas into the SRU. The question to be answered was whether the reactors could sustain the Claus reaction if the catalyst was not hot when process gas began flowing into the reactors. Consider what happens when hot process gas containing H_2S and SO_2 begins flowing across cold catalyst:

(1) Reaction initiation temperature is not critical. It is widely known that the Claus reaction can take place at ambient temperature (albeit slowly) even without a catalyst present. For instance, sulfur fouling is a common problem in sour gas pipelines connected to vacuum gathering systems because air leaking into the system allows oxygen and H_2S to react to form sulfur.

(2) The H_2S and SO_2 immediately begin to react to form sulfur. Because the catalyst is cold, the sulfur as it forms will condense (perhaps even solidify) on the catalyst, blocking the pores of the catalyst and rendering it inactive.

(3) The Claus reaction is very exothermic, so the catalyst begins to heat up due to the heat release from the reaction. The latent heat of the condensing sulfur and the sensible heat of the hot process gas also help heat the catalyst.

Thus, there are two competing processes taking place. The condensing sulfur is beginning to deactivate the catalyst bed, while the heat of reaction, latent heat, and sensible heat are heating the catalyst to get it above the sulfur dewpoint so that it stays active. Ortloff made calculations for several typical plant designs using reasonable assumptions to compare the catalyst heating rate with the sulfur deposition rate on the catalyst, and concluded that the temperature of the top layer of catalyst would increase above the sulfur dewpoint before enough sulfur deposited in the catalyst pores to completely deactivate the catalyst. Encouraged by these calculations, Ortloff then attempted a plant startup with cold catalyst beds and demonstrated that the procedure worked.

Application of Cold Reactor Bed Startup

The key to applying this cold bed startup procedure is to bring all the other equipment in the SRU (furnace, reheaters, condensers) up to operating temperature before commencing acid gas flow. For the furnace, its boiler, and the first sulfur condenser, this is accomplished by combusting fuel gas in the acid gas burner much like in a conventional plant. However, these combustion products are diverted to the incinerator before reaching the first catalyst bed as shown in Figure 1. Since the combustion products do not flow through any of the reactors, the burner can be operated with excess air to control the desired temperature in the furnace and follow the prescribed heating schedule. With no flow to the reactors, there is no chance of starting a sulfur fire in the catalyst beds, so there is no need to operate the burner close to stoichiometric and risk forming soot. There is also no need to add large volumes of steam or nitrogen to the furnace to control the furnace temperature as is necessary for conventional plants.

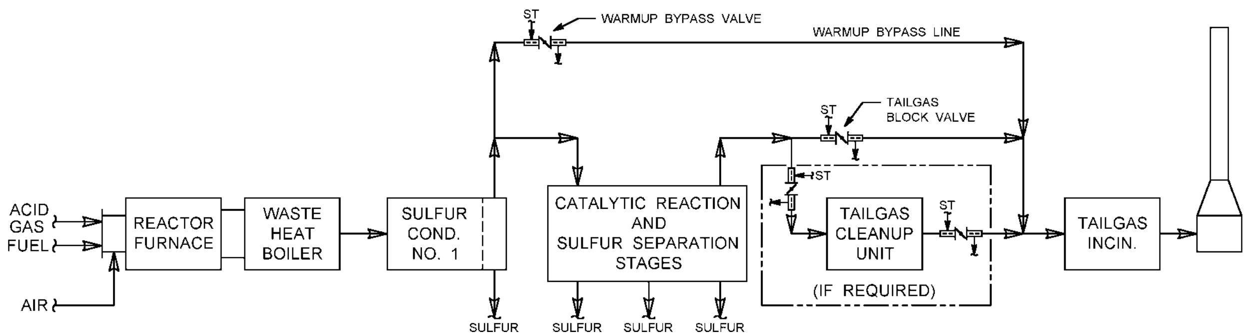

Figure 1 — Cold Reactor Bed Startup Design

Before flowing to the incinerator, the hot combustion products flow through the waste heat boiler and the first sulfur condenser. As the gas flows through the tubes in these boilers, it heats the water in the boilers and begins to generate steam. For smaller SRUs where the reheat pass tubes are incorporated in a common shell with the waste heat boiler and all the sulfur condenser passes are in another common shell, this brings all the heat exchange surfaces up to operating temperature. For plants with the different services in separate shells, the high pressure steam produced by the waste heat boiler is used to heat the reheater tubes and to circulate and heat the water in the other sulfur condensers (using steam-driven eductors, for instance). Once the furnace is up to operating temperature, the tailgas block valve to the incinerator can be opened and the warmup bypass valve closed, acid gas flow can be established into the sulfur plant, and fuel gas firing discontinued to bring the sulfur plant on-line.

The design features incorporated in this cold bed startup technique offer the following advantages over conventional plant designs:

1. The catalyst beds are not exposed to warmup gases containing free oxygen, eliminating sulfur fires in the catalyst beds that cause overheating damage to both equipment and catalysts.

2. The catalyst beds are not exposed to warmup gases that contain free carbon (soot), eliminating contamination and plugging of the beds with soot.

3. The catalyst activity level remains high for much longer. Deactivation has been shown to be caused primarily from sulfate contamination of the catalyst surface. The sulfation rate is very much lower when the catalyst is not exposed to typical warmup conditions and gases.

4. The sulfur plant can be kept on hot standby, firing on fuel gas, without exposing the catalyst beds to overheating, carbon deposition, or sulfation damage. The hot fuel gas combustion products (and other design features) keep all process heat exchange surfaces at normal operating temperatures. Since most corrosion damage in sulfur plants occurs when the plants are allowed to cool down and stand cold, these cold bed startup design features can greatly extend the service life of sulfur plants which require considerable standby time.

All of the Ortloff-designed sulfur plants built since 1970 (more than 50 now) have been designed for cold bed startup. The "coldest" startup so far has been at the plant installed in Tioga, North Dakota in 1991. This plant has been successfully restarted during the winter after most of the bed temperatures had fallen below 0°F (-18°C). The more severe test of the startup technique, however, has been restarting plants at low processing rates, since heat losses to the surroundings are much more significant and channeling through the catalyst beds is much more likely when operating at low flow rates. Figure 2 shows a plot of the reactor bed temperatures for a 50 T/D plant during its initial startup with cold reactor beds, operating at about 25% of design throughput due to lack of feed. Even at this feed rate (and with adsorbed water still in the catalyst initially), the top of the catalyst bed was up to operating temperature within 3 hours after acid gas flow began.

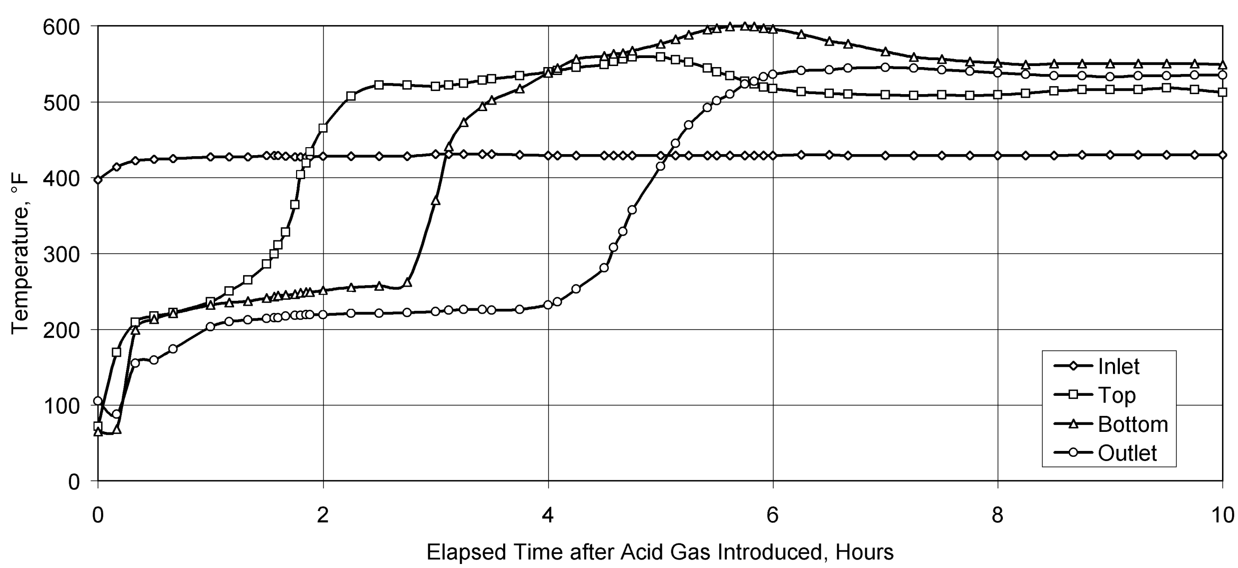

Figure 2 — Catalyst Bed Temperatures during Startup

The plants that have consistently employed this cold reactor bed startup technique have obtained much longer service lives from the catalyst charges in the reactors than comparable units using conventional startup procedures. We believe this is directly related to the much lower incident rate of exposing the catalyst beds to oxygen (which causes sulfation and fires) and to combustion products (which causes carbon fouling and plugging). At least two of our plants, one in a gas plant and the other in a refinery, have gone nine years before replacing the original catalyst charge.

Conclusions

Using the cold reactor bed startup procedure not only simplifies startup, it improves sulfur plant reliability and prevents interruptions in refinery or gas plant production. Cold reactor bed startup is one of many design concepts that have been developed over the past 30 years at Ortloff to improve the reliability and operability of sulfur recovery facilities.[2] Although many of these concepts are quite different from the usual "industry practice", we have found that in most cases these alternative design concepts not only improve reliability, but also reduce the capital and operating costs of these units.

References

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