The CONTACTOR™

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Causes of Claus Catalyst Deactivation

The catalytic stages in a Claus unit accelerate the Claus reaction at lower temperatures where equilibrium is more favorable (Figure 1). Catalyst activity sets the sulphur recovery performance of the unit. When loading fresh catalyst into the vessel, the catalyst has maximum surface area and activity. However, on start-up, the catalyst is immediately exposed to a number of possible deactivation mechanisms, many causing irreversible damage. While the focus of this article is primarily on conventional activated alumina, the same deactivation mechanisms generally apply to all Claus catalysts, e.g., alumina and titanium dioxide. Put simply, the activity of a given Claus catalyst is set by the surface area of macro- and microporous surface structure that is accessible to the reactants, and that must also allow the reaction products to escape from the pores.

Hydrothermal Aging

Hydrothermal aging is an unavoidable deactivation mechanism that causes an unrecoverable loss in surface area. Temperature changes in the presence of water vapor cause constant expansion and contraction of the catalyst, warping and misshaping its surface, and causing a permanent destruction of micropore structure. This is a normal aging process for the catalyst and occurs over an extended period of time. Fresh catalyst has a surface area of approximately 350+ m^2/m^3. Over several months in service, the surface area will decrease to approximately 250 – 300 m^2/m^3. Under normal operation, the surface area will then remain largely unchanged, with the potential to last quite a long time if operated properly. Hydrothermal aging tends to occur uniformly throughout the converter bed.

Sulphur Condensation

If the converter is operated at or below the sulphur dewpoint, liquid sulphur can accumulate within the catalyst's pores, blocking access. This is typically associated with a problem in the upstream reheater operations. It can be reversed simply by increasing the temperature within the converter beds, to revaporize the condensed sulphur. Sometimes this is easier said than done. For example, the designer may have failed to provide enough margin to the reheater to cover this operating scenario, or the plant may be operating above its originally intended design. In such cases, recovery can be restored by starving the Claus bed of a reactant (typically by operating at high H_2S:SO_2 ratio) or by cutting rates to the unit to yield a hotter reheater outlet temperature.

Excessive sulphur entrainment from upstream condensers and blocked sulphur rundown lines can also increase the likelihood of reaching the sulphur dewpoint ***within*** the catalyst bed (not just at the outlet of the converter). It's also notable that some sulphur condensation within the micropore structure is almost unavoidable because the bulky S_8 molecule formed is larger than some of the micropores. The S_8 molecule effectively becomes irreversibly stuck, being unable to vacate the catalyst pores. SulphurPro® evaluates the dewpoint temperature margin ***within*** the catalyst bed, which is crucial to predicting deactivation by this particular mechanism.

The Claus reaction is favored at low temperatures (Figure 1) and several Claus processes were invented to take advantage of sub dewpoint operation, e.g., the Cold Bed Adsorption and Sulfreen™ processes. The trick is to regenerate the catalyst (vaporizing and removing the condensed sulphur) before the catalyst surface becomes significantly deactivated. This is typically done online by using multiple reactor vessels cyclically switched between adsorption and regeneration modes.

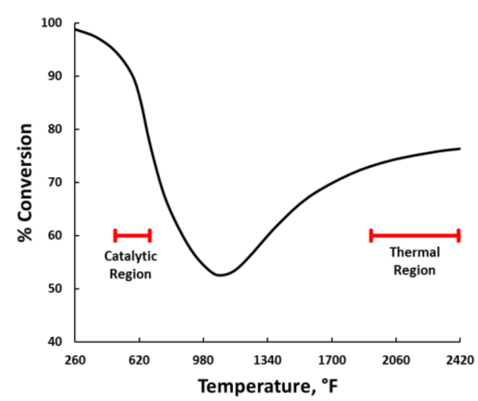

Figure 1. Thermal Capabilities of the Claus Process

Soot Formation

Sooting is the deposition of carbon within the catalyst pores, which effectively blocks the macropores and makes access to the mesopores and micropores impossible. It most commonly occurs when sub- or near-stoichiometric natural gas firing is used on startups and shutdowns, or by improperly operating inline reheat burners. This type of deactivation typically occurs at the top (or inlet) of the catalyst bed and creates a rigid crusty structure. It causes not only loss in catalyst performance, but increased pressure drop through the converter vessel, thus lowering hydraulic capacity, too.

Performing a sulphur wash can help remove these particulate fines from the surface of the catalyst. It is becoming a more common practice performed online to help mitigate the increased pressure drop. The practice was pioneered by Saudi Aramco [Al-Haji, M.N. & A-Adab, A.M., *Sulfur wash removes soot from Claus catalyst bed online,.* Oil and Gas Journal, 99, 54–59 (2001)]. Another common practice done offline involves "raking" the catalyst bed following a sooting episode to help break up the crust. Skimming off the top layer can also be done with similar results. Both methods are bandaid fixes for a more serious problem. To help prevent soot formation in the first place, a preferred practice is to use tempering steam to scavenge the soot when firing natural gas. A minimum steam to natural gas mass ratio of 0.5 is generally sufficient for this purpose. A sooty flame is typically tallow to orange in color. Tempering steam causes the flame to "disappear", something operators tend not to like.

Carsul

If hydrocarbons leave the Reaction Furnace, they can crack and combine with sulphur across the catalyst surface, forming a tenacious carbon-sulphur polymer (hence the term Carsul). Similar to sooting, this coats the catalyst, blocks the macropores and prevents access to the mesopores and micropores. Cracking tendency is worst at high operating temperatures, especially above 450°F (232°C). BTEX is particularly nasty in this regard as the cracking occurs deeper in the catalyst pore structure. Carsul formation can occur with any C_3+ hydrocarbon. Since converter beds operate with a temperature ***rise***, this type of deactivation often progresses from the bottom to the top of the catalyst bed. Deactivation by Carsul is permanent, but it's completely preventable by keeping hydrocarbons out of the acid gas feeds to begin with or by using higher operating temperatures in the Reaction Furnace to destroy hydrocarbons. Activated carbon and silica gel beds have historically been used to scavenge BTEX out of lean acid gas feeds because it's difficult to produce Reaction Furnace temperatures necessary to destroy BTEX by combusting lean acid gas.

Sulfation

Sulfation results from the interaction of SO_2 and H_2O on the catalyst surface, causing gradual buildup of sulfate, most commonly in the 2nd and 3rd converter beds. It reduces the effective surface area of the catalyst and can be either reversible or irreversible. The first type can be reversed by operating the Claus unit H_2S rich (H_2S:SO_2 ratio of 15:1 or higher) and elevating the converter bed temperature 30–50°F (17–28°C) above normal. Reversible sulfation can become irreversible.

Torching

Torching occurs from a "runaway" sulphur fire when free oxygen from the upstream Reaction Furnace or Inline Reheat Burner contacts elemental sulphur on the surface of the catalyst above sulphur's autoignition temperature (>392°F, 200°C). Rapid, permanent deactivation results. As the bed "burns", a host of other unit problems can result from sulfurous acid corrosion and deposition of the "sulfacrete" product. Prior to a shutdown, some operators practice a controlled form of bed burning to remove pyrophoric iron sulfide and combustible sulphur, preparing the converters for safe entry. If a passivation step must be done, it is advisable first to heat soak the bed on sub-stoichiometric natural gas firing until sulphur is removed from the catalyst.

Simulating Catalyst Aging

Sulphur-Pro can account for the behavior of an aged catalyst. Figure 2 shows three measured converter temperature profiles vs. simulation. Aging can have a marked effect.

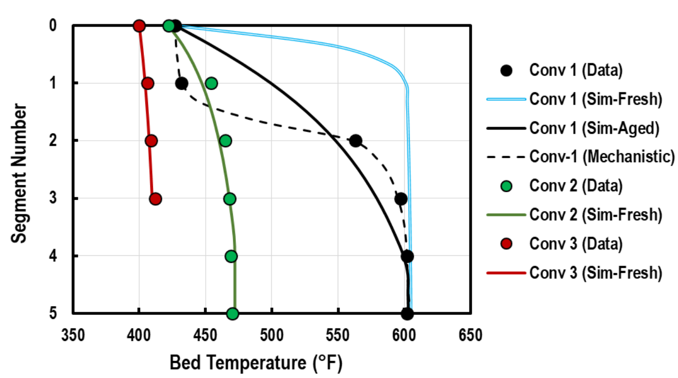

Figure 2 Converter Temperature Profiles

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