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Claus Converters, Catalyst Deactivation, and Approach to Modeling

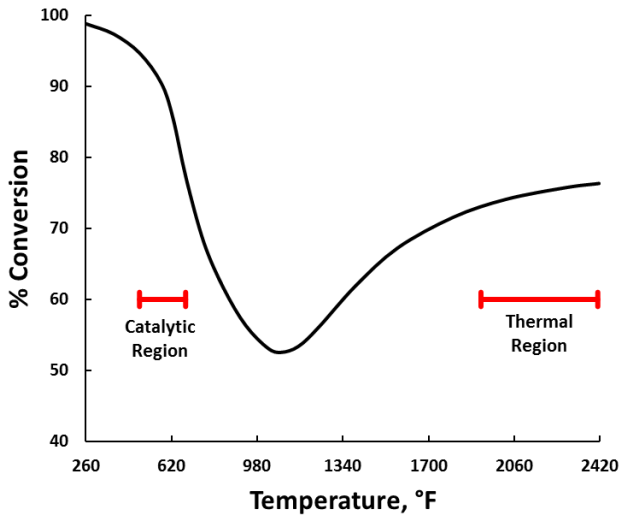
The Modified Claus Process involves converting H_2S to elemental sulphur through indirect oxidation with SO_2. In order to do this, the acid gas entering the Sulphur Recovery Unit (SRU) needs to be combusted to turn 1/3 of the H_2S into SO_2 through Reaction (1). The gas, now containing both H_2S and SO_2, will be brought towards equilibrium with the reaction products being sulphur and water through Reaction (2). The sulphur is then removed, through cooling the gas and condensing the sulphur, to allow the reaction to advance. This takes advantage of Le Chatelier's principle; by removing the reaction product, equilibrium will shift forward towards the product side of Reaction (2). The process is repeated anywhere from 1–3 times in series. For Reaction (2) to achieve equilibrium at lower temperatures, a catalyst is required, and Claus catalytic converters, which contain the catalyst beds, are the key to this process.

$$\textbf{Reaction (1)}: \quad H_2S + \frac{3}{2}O_2 \rightarrow SO_2 + H_2O$$

$$\textbf{Reaction (2)}: \quad 2H_2S + SO_2 \rightleftharpoons \frac{3}{x}S_x + 2H_2O$$

To achieve the best possible sulphur conversion, the Claus catalyst must be at its peak kinetic potential. The two main ways to ensure this are by choosing the right catalyst bed operating conditions and maintaining catalyst activity.

Figure 1. Thermal Capabilities of the Claus Process



The operating diagram in Figure 1 shows that conversion is favored by Claus reaction equilibrium at low temperature. It is possible to approach 100% conversion by operating the converter beds at very low outlet temperature. However, there are practical limitations. First, reaction kinetics are slower at lower temperatures – the reactions may be so slow that the favorable equilibrium is never realized. Second, the liquid sulphur dewpoint can be reached, resulting in one form of catalyst deactivation further discussed later. The final limitation involves COS and CS_2 hydrolysis which requires higher temperatures for effective conversion. COS and CS_2 hydrolysis are not necessarily reflected in Figure 1.

Claus Catalyst Deactivation Mechanisms

Claus catalyst activity plays a major role in determining the sulphur recovery performance of the unit. There are many factors that determine catalyst activity. On first loading the catalyst into the vessels, the catalyst is considered fresh and at its maximum surface area and activity. However, upon start up of the SRU, the catalyst is immediately subjected to a number of possible deactivation mechanisms.

An unavoidable deactivation mechanism is hydrothermal aging which is the unrecoverable loss of surface area. This is caused by the loss of micropore structure from constant expansion and contraction of the catalyst with temperature changes in the presence of water vapor. It is a normal aging process for the catalyst, and it happens over an extended period of time. Newly loaded catalyst has a surface area of approximately 350+ m^2/m^3. After 1–3 months, the surface area will decrease to approximately 250–300 m^2/m^3. Barring upsets and harsh operating conditions, the surface area will then remain largely unchanged in this state. If operated properly, Claus catalyst can last for quite a long time.

If the Claus converter is operated at or below the sulphur dew point, liquid sulphur begins to accumulate within the pores of the catalyst, blocking access to the active sites on the surface. This is a completely *reversible* deactivation mechanism because increasing the temperature in the converter beds vaporizes the liquid sulphur and restores activity. Excessive sulphur entrainment from upstream sulphur condensers and blocked sulphur rundown lines can increase the likelihood of reaching the sulphur dewpoint within a catalyst bed. Referring to Figure 1, the Claus reaction is favored at low temperatures and operating below the sulphur dew point can be deliberately done to boost conversion. The trick is to regenerate (vaporize and remove) the sulphur from the catalyst pores before the catalyst surface is significantly deactivated. A family of sub-dewpoint Claus processes was invented with this in mind; examples include the Cold Bed Adsorption (CBA) and Sulfreen™ processes. It is important to note that the dewpoint can sometime occur *within* the catalyst bed — it is not always reached at the outlet of the converter. The SulphurPro™ model

in the ProTreat® simulator evaluates the dewpoint temperature margin **within** the catalyst bed, which is crucial in predicting this particular deactivation mechanism.

Sooting is another form of deactivation, and is caused by carbon deposition within the catalyst pores. Sooting typically happens from sub- or near-stoichiometric natural gas firing on startups and shutdowns, or by improper operation of inline reheat burners. Because this type of deactivation occurs from top to bottom of the bed, a common practice is to "rake" the catalyst bed following a sooting episode. This requires a plant shutdown and costly downtime. A better practice is to use tempering steam to scavenge soot while firing natural gas. Using a steam to natural gas mass ratio of 0.5 is generally sufficient for soot scavenging purposes. The flame resulting from soot is yellow to orange in color. Tempering steam causes the flame to "disappear", and operators tend not to like this.

Carsul formation is yet another way that Claus catalyst can become inactive. When unburned or partially combusted hydrocarbons leave the Reaction Furnace, they can crack and combine with sulphur across the Claus catalyst surface to form a tenacious carbon-sulfur polymer (hence the term Carsul). Cracking tendency is worst at high operating temperatures, especially above 450°F (232°C). BTEX is particularly nasty, but Carsul formation can occur with any C_3+ hydrocarbons. Since converter beds operate with a temperature rise, this type of deactivation is often from the bottom to top. Permanent deactivation results, but it is completely preventable by keeping hydrocarbons out of the acid gas feeds to begin with or by ample operating temperature in the Reaction Furnace. Activated carbon and silica gel beds have been used for leaner acid gas feeds containing BTEX that are unable to produce the Reaction Furnace temperatures necessary to adequately destroy BTEX.

Sulfation is caused by the interaction of SO_2 and H_2O on the surface of the catalyst and can be either reversible or irreversible. The reversible type can be recovered by operating the Claus unit H_2S rich (at an H_2S:SO_2 ratio of 15:1 or higher) and by elevating the converter bed temperature 30 to 50°F (17 to 28°C) above its normal operating temperature. If it is not taken care of, the reversible form of sulfation can become irreversible over time.

For want of a better description, the final form of deactivation is best summarized by the word "torching". Torching occurs when free oxygen from the upstream Reaction Furnace or Inline Burner contacts elemental sulphur on the surface of the catalyst at temperatures exceeding the auto-ignition temperature of sulphur. Rapid and permanent deactivation results. As the bed "burns", a host of other unit problems can result from sulfurous acid corrosion and the "sulfacrete" corrosion product. Prior to shutdown, some operators practice a controlled form of bed burning to prepare the converter vessels for safe personnel entry. The intent is to convert pyrophoric iron sulfide and remove combustible sulphur. 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 no longer present on the catalyst surface.

Approach to Modeling:

The ProTreat® SulphurPro™ model accounts for kinetics of the Claus reaction, as well as COS and CS_2 hydrolysis across alumina catalyst beds. Both macroporosity and surface area are accounted for in the proprietary model, with the current "alumina" option being for 2nd and 3rd generation 3x6 mesh activated aluminas.

Figure 2. Kinetic Activity Parameter and Predicted Profiles

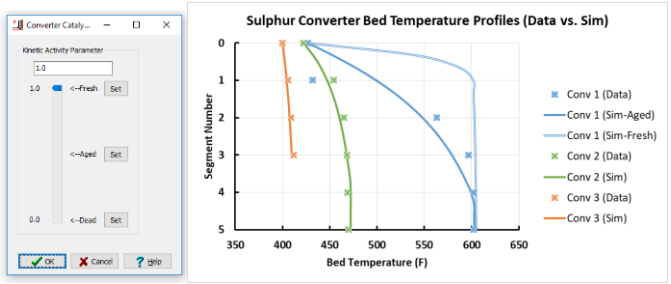
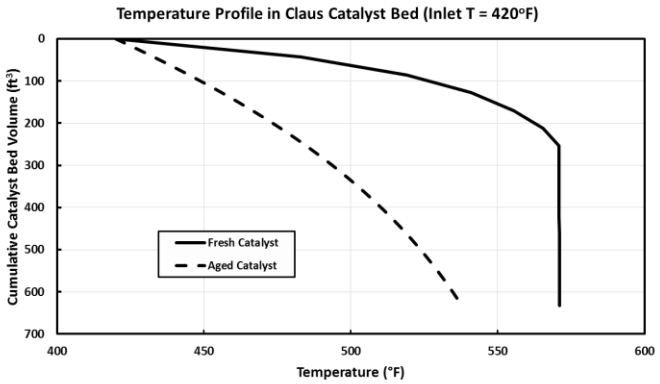


Figure 3. Fresh vs. Aged Catalyst Activity in SulphurPro™



Figures 2 and 3 show the kinetic activity parameter and how this can be adjusted to account for catalyst deactivation. Figure 2 compares the SulphurPro predicted temperature profiles with data from an operating plant in which temperature measurements were available in all three Claus converters. The 1st Converter's measured temperature profile shows some top-down deactivation. Accounting for this was critical to matching this plant's temperature profiles and sulfur reccovery performance. The performance benefits of replacing the catalyst can then be assessed by comparison to the predicted performance with fresh catalyst. Armed with this information, the plant engineer is better equipped to recommend whether the capacity and emissions benefits to the SRU/TGU complex are worth taking the unit down early for a catalyst change-out, replacing the catalyst at the next scheduled turnaround, or leaving the unit alone.

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