The CONTACTOR™

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Sneaky SO_2 Breakthroughs

SO_2 breakthroughs are one of the most damaging and devastating process upset events that can occur within a Sulphur processing unit. The damage, if not caught and mitigated in time, can affect both the Quench water loop and Tail Gas Unit (TGU) amine section. Corrosion and plugging are the most common for the Quench water loop while solvent degradation and loss of selectivity leading to high CO_2 recycle rates are most common if the problem so severe it makes it into the TGU amine section. The hydrogenation reactor is responsible for converting SO_2 back into H_2S (subsequently absorbed and recycled back to the front of the SRU) and is the most critical operation for preventing SO_2 breakthroughs. SulphurPro has a first-rate hydrogenation reactor module which allows a breakthrough to be caught early in its evolution.

How Breakthroughs Happen

In the Sulphur Recovery Unit (SRU) sulphur compounds are recovered as elemental sulphur. The various units and the SRU as a whole are less than 100% efficient so the small amount of unrecovered sulphur is emitted to atmosphere where it is tracked and traced for compliance with sulphur emission standards.

The SRU converts H_2S into elemental sulphur via a thermal stage and two or three catalytic stages.:

$$H_2S + \frac{3}{2}O_2 \rightleftharpoons SO_2 + H_2O \qquad \text{Thermal}$$

$$2H_2S + SO_2 \rightleftharpoons \frac{3}{x}S_x + 2H_2O \qquad \text{Catalytic}$$

The TGU processes the off-gas from the SRU, and is a multistep process commencing with the hydrogenation reactor. Here non-H_2S sulphur species are converted to H_2S. This catalytic stage is also responsible for continuing the Claus process and it water-gas shifts carbon monoxide into hydrogen *which helps aid the hydrogenation reactions* along with reducing CO emissions. The reactants in the hydrogenation reactor are:

- COS, CS_2 – hydrolysis on alumina
- SO_2, S_x, COS, CS_2 – hydrogenation on Co/Mo
- CO – water gas shift on Co/Mo

The process chemistry is complex with several parallel reactions plus reactions between SO_2 and other reduced sulphur species.

The next step is quenching the hot gas, removing both heat and water-of-reaction. This is the first line of defence when facing an SO_2 breakthrough. The pH of the quench water is monitored and caustic (or sometimes ammonia) is injected when the pH drops below a certain threshold in order to neutralize and absorb the acidic SO_2 before it makes its way to the next section of the TGU, the amine circuit. The amine selectively recovers H_2S and allows as much CO_2 as possible to leave the system. The recovered H_2S is stripped from the solvent and recycled to the front end of the SRU. Using a TGU gives sulphur recovery efficiencies of around 99.9%.

An uncompromising requirement of the catalyst in the hydrogenation reactor is that SO_2 be fully converted to prevent residual SO_2 from entering the quench circuit where fouling, corrosion will occur, and the amine circuit where amine deactivation and loss in selectivity occur. High conversion of COS, CS_2, and mercaptans are also required as the hydrogenation reactor is the last line of defence for these compounds before they are vented to atmosphere. Amines generally have very little affinity towards mercaptans and will not remove much from the gas.

SulphurPro® Hydrogenation Reactor Model

The hydrogenation reactor model implemented into OGT|SulphurPro® is reaction kinetics and mass transfer rate-based. The 11-reaction set includes all major reactions as well as the side-reactions that occur in parallel, and pore diffusion within the catalyst pellets. A key part of the model is the inclusion of catalyst aging and poisoning. Catalyst activity determines the performance of the hydrogenation reactor, and deactivation of the catalyst occurs through aging and poisoning. The gradual loss of catalytic rate is inevitable that must be fully accounted for and addressed in the initial design of a TGU. This will be the subject of a separate future issue of The Contactor™.

Case Study

The case outlined here is based on an operating refinery SRU in North America. The unit processes both Amine Acid Gas

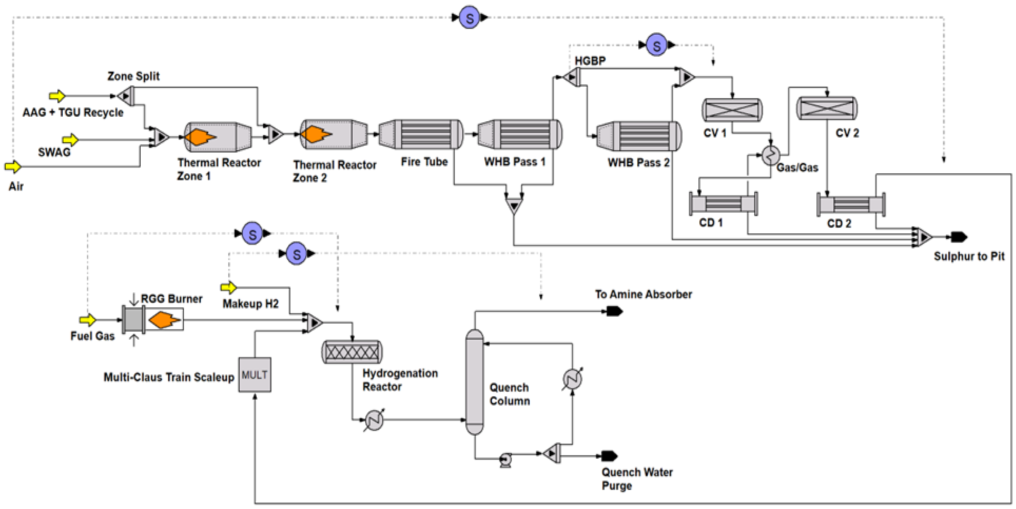

Figure 1 SRU and Front End of TGU (Reduction+Quench)

(AAG) and Sour Water Acid Gas (SWAG) as shown in Figure 1. The main complaint by the operators was that SO_2 breakthrough-like symptoms were observed for years through cloudy quench water, frequently plugged and bypassed quench water filter elements, and thiosulfates in the downstream TGU amine section. However, they were never able to detect any SO_2 in the feed gas of the Quench column even with the help of expert, specialized, analytical testers to help troubleshoot. To get a deeper understanding of how SO_2 breakthroughs occur and to pin-point what might be happening in this particular plant, a set of case studies was performed to gauge how small changes in the operating condition of the SRU could affect the performance of the TGU hydrogenation reactor.

Findings

The base case used test run data provided by the operating plant with the catalyst age set to the specific number of months the catalyst bed had been operating (controls catalyst hydrothermal aging) and the specific poisoning agents that the catalyst bed had seen. We then carefully compared the test run CO/COS and the bed temperature profiles to ensure the model was an accurate representation of the plant performance at the time of the snapshot. Once validated, upset conditions were simulated by placing the Claus air on manual and stepwise increasing its flowrate. Table 1 shows simulation results.

Table 1 Effect of Excess Air on TGU Reactor Performance

Excess Air	SO_2 in Rx Outlet	Quench O/H H_2	Quench Water pH	Quench O/H SO_2
(%)	(ppmv)	(Mole %)	pH	(ppmv)
Base	5.6	2.1	773	0.013
1%	12.9	1.8	7.47	0.031
3%	74.7	1.0	7.09	0.232
5%	414.2	0.4	4.63	367
7%	1473	0.1	3.83	1910
10%	4014	0.02	3.19	5516

Upon obtaining a representative case, the model showed that with the given test run data, there was 2 to 11 ppmv of SO_2 slipping from the Hydrogenation Reactor into the Quench column. This varied in the model depending on the poisoning agents assumed in the poor-quality reducing hydrogen. The amount of hydrogen in the quench overhead was right at the desired 2.0% level and did not indicate anything wrong with the hydrogenation reactor.

This being a refinery, the SRU is processing ammonia, some of which ends up in the quench water loop and acts to buffer against small (but limited) amounts of SO_2. The ammonia is able to buffer against 1% excess air, but 5% excess overwhelms it, so the SO_2 level escalates to 100s and 1,000s of ppmv, and this enters the amine system. The quench water, which is usually at a pH of 7–9 because of low CO_2 levels and ammonia buffering, quickly turns acidic.

In this particular case, the baseline pH of the quench water was around 7.5 which is right in line with the expected 7 to 9 range. As the amount of SO_2 slip from the hydrogenation reactor increases, the pH does not drop very sharply because of the buffering ammonia, and so pH was not necessarily a good indicator of an SO_2 breakthrough.

As shown in Table 1, the amount of SO_2 slipping through the reactor exponentially increases with small step changes in the amount of excess air feeding the unit. In the base case (and even the 1% excess air case), this small amount of SO_2 would be undetectable even with the sophisticated equipment of the some of the analytical companies. The SulphurPro model suggested the plant was experiencing a chronic SO_2 leak due to the aged *and poisoned* hydrogenation catalyst. Aging alone was insufficient to account for our observations.

By using the rigorous rate-based kinetics model with catalyst aging and poisoning implemented in SulphurPro®, a long-term reliability and operability problem that had gone unresolved for many years was systematically identified and resolved. This particular tool can be used not only to study intervention techniques, but also mitigation methods, too.

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To learn more about this and other aspects of gas treating and sulphur recovery, plan to attend one of our training seminars. Visit https://www.ogtrt.com/training for details.