# Sulfur Processing Operations during Startup, Shutdown, and Turndown

G. Simon A. Weiland and Nathan A. Hatcher
Optimized Gas Treating, Inc.
212 Cimarron Park Loop
Buda, TX 78610

## Abstract

Startup, shutdown, and turndown operations are hard to consider fully at the outset of a project. The primary focus is usually on providing a design that accommodates the worst possible steady-state operating conditions. Attention given to startup, shutdown, and turndown — conditions that can cause the most damage to plant equipment — is usually low and often given at the last minute, if at all. The extent to which the hardware can be turned down is often not known until equipment bids have been received, and recycle in the work flow to the process engineering department is required to confirm that the hardware will perform under all expected operating conditions. In fast tracked projects sometimes only superficial attention is given to these critical steps, and the level of detail required in a complete evaluation with new process designs is inadequate.

Mass and heat transfer devices as well as material transfer equipment and instrumentation behave differently under turndown conditions, and not always in ways that are desirable. The present work is a case study of the startup, shutdown, and turndown operations of a refinery gas treating and sulfur processing train and focuses on changing demands placed on the process equipment.

## Introduction and Background

Sulphur recovery units (SRU's) are designed to meet a specific set of targets given an initial set of premises such as feed flowrates, feed composition, feed temperatures, and pressure. During the design phase, considerations are generally given to different scenarios such as varying feed quality, feed rate (turndown), equipment aging (exchanger fouling), and catalyst aging to help assess the robustness of the design. However, startups and shutdowns arguably cause the most damage to an SRU through thermal cycling of the process equipment, and it is these very conditions that are often overlooked or not given much thought. Thermal cycling affects the reliability of the Waste Heat Boiler (WHB) most notably by degrading the tubesheet system, which includes the refractory, ferrules, the tubesheet itself, the tube-to-tubesheet joints, and the tubes. Through proper design, operating practices, and maintenance procedures, the Reaction Furnace and WHB system can have life expectancy in excess of 20 years. However, with an inadequate design, poor operating practices, and poor maintenance, it could be as short as two to three years [1, 2]. Being able to model accurately varying feed quality, feed rate, exchanger fouling, and catalyst aging can provide better understanding of the effects of these parameters.

## Startup Operations

Procedures for starting up an SRU vary slightly between bringing an existing unit back online after a shutdown versus a green unit that has never before seen sulphur. In overly-simplistic terms, the following steps are usually taken:

1. Light the pilot
2. Light the main burner
    a. If the unit has never seen sulphur, or if the refractory is "green", then excess air is typically used to control the rate of refractory heat up per the manufacturer guidelines with regard to the maximum temperature change per hour for the refractory to minimize the potential for refractory thermal shock and the consequent damage. Considerations in some jurisdictions for maintaining a TGU downstream in operation that is always "coupled" to the SRU may preclude excess air operations to prevent damage to the Co/Mo catalyst if presulfiding has been previously conducted.
    b. If the unit is being brought back online after processing sulfur previously, then excess air is forbidden in order to prevent sulfur fires. The procedure involves firing natural gas and air at 90% to 95% of stoichiometric at a hydraulic load corresponding to *at least* 30% of the design operating rate on acid gas. A convenient average hydraulic load for the SRU that is often taken for a basis is the molar flowrate as measured at the outlet of the first condenser. The natural gas will then gradually be replaced with acid gas until the unit is running on only acid gas and air at the 30% design rate.
3. Bring in acid gas when the unit is properly heated up and stable.

Most flowmeters start losing accuracy at flows below 25% turndown so setting the limit for startup at 30% ensures flowrates will be well within the range of most instruments. Having some hydraulic back pressure on the unit also helps to maintain feed gas and air control valves in operable positions. Burner backfiring is a serious issue at turndown because it causes damage to the burner tip which can then lead to an irregular flame pattern, hot spots, and ultimately burning a hole in the Reaction Furnace wall.

## Shutdown Operations

Simplistically put, shutdown procedures, can be considered the direct opposite of startup. The unit is first turned down to approximately 30% of the design rate and the acid gas is gradually replaced with natural gas until the unit is operating on only natural gas, tempering steam and air. This period of operation is also referred to as hot standby. The purpose here is to keep the equipment hot and remove the elemental sulfur from the plant equipment either in preparation for a true shutdown or to keep the system idling.

## Turndown Operations

It is normal for an SRU to operate at below design flowrates. More often than not, the initial operating conditions (which include flowrates) change after construction and commissioning, as well as during operation of the unit. Ensuring that the unit will perform adequately under these non-design conditions is crucial to successful operation.

Heat losses from plant equipment also become more significant at turndown, and separations equipment may not perform as advertised either. In a sulfur condenser, for example, fogging has been reported at low mass velocities (<1 lb/sec-ft$^2$) $^{(3, 4)}$. Fogging is a phenomenon in which submicron mist is formed in the bulk vapor versus normal film condensation on the condenser tubes. This mist is so fine it evades conventional mist elimination devices.

An important part of turndown operations is knowing whether the plant equipment is operating safely and reliably. Here, we use an example of how process simulation can complement plant operations.

## Case Study

A series of case studies was performed to analyze startup and shutdown operations as well as the effects of turndown on the SRU. The Claus Unit analyzed was a typical 2-stage unit in a refinery setting processing both sour water acid gas and amine acid gas at a combined design flowrate of 125 TPD as shown in Figure 1 and Table 1. The heat exchange units, such as WHB and condensers, were simulated in rating mode to assess accurately the effects of operating at off-design rates. All cases were simulated using SulphurPro$^{TM}$, a kinetic rate and heat transfer rate based sulphur recovery simulator.

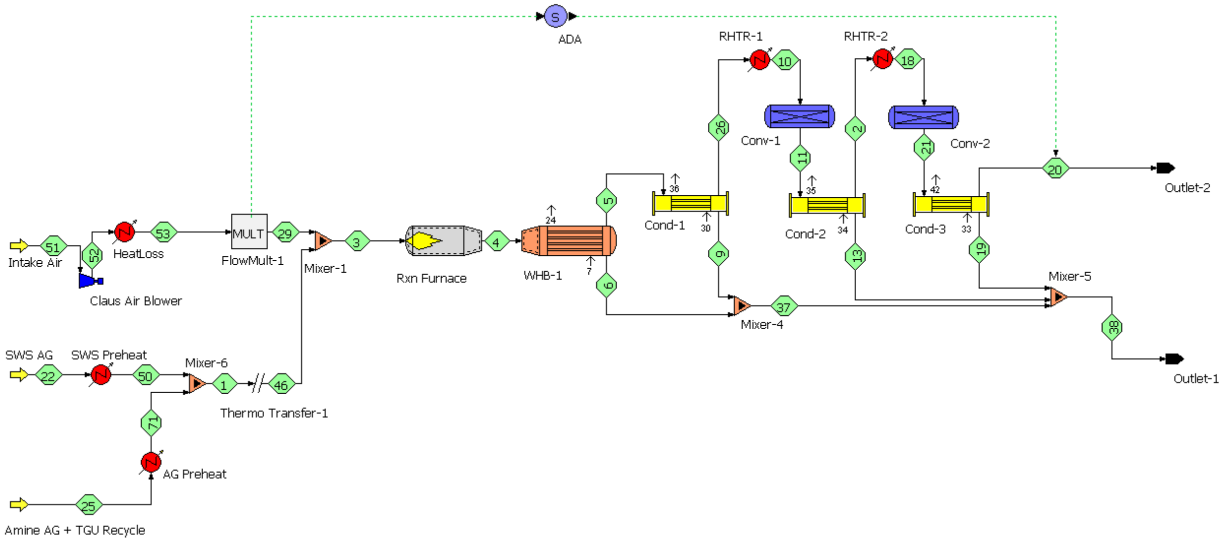

Figure 1. SulphurPro$^{TM}$ PFD for 2 Stage Claus Unit Processing Amine Acid Gas and Sour Water Acid Gas

Table 1. Feed Conditions for Amine Acid Gas and Sour Water Acid Gas (mole %)

| | Amine Acid Gas | Sour Water Acid Gas |
|---|---|---|
| **$H_2O$** | 5.28% | 22.19% |
| **$H_2S$** | 87.14% | 35.01% |
| **$CO_2$** | 6.63% | ----- |
| **$NH_3$** | ----- | 42.79% |
| **$CH_4$** | 0.947% | ----- |

For the first case study, the unit simulation was run in two turndown scenarios; one at 75 TPD (60% of design) and the other at 40 TPD (30% of design). The performance of the unit, and specifically the exchangers, was assessed at each turndown step.

For the second case study, the unit was assessed at a point corresponding to half way between the startup/shutdown procedures. Natural Gas and Acid Gas (from both Amine Acid Gas and Sour Water Acid Gas sources) were both sent to the Claus unit in equal amounts (50% each) at a combined hydraulic load that was equal to the hydraulic load at 30% of the design rate on acid gas only. This gave a point midway between hot standby (natural gas only) and turndown on acid gas (40 TPD or 30% of design).

## Results – Turndown and Basic Startup Cases

As seen in Table 2, as the unit is turned down from 100% to 60%, and then 30%, the most notable change is in the WHB operating conditions. At 30% turndown, the peak heat flux is reduced to nearly half of the base case of 100% throughput. This results from the severely reduced mass flux through the unit. The overall sulphur conversion, sulphur recovery, and $CS_2$ in the tail gas do not seem not to be highly affected. Pressure drop, although not directly calculated, reduces significantly with turndown.

Hydrogen in the Claus tail gas drops quite significantly from the Base Case design as turndown progresses. This can have significant impacts on the performance and reliability of a reduction-quench-amine type Tail Gas Treating Unit (TGTU) downstream. The reducing gas demand is increased per unit volume of feed gas as the unit is turned down, meaning either more external hydrogen or more natural gas must be combusted substoichiometrically in the TGTU Reducing Gas Generator (RGG) at turn down. Insufficient hydrogen increases the risk of $SO_2$ breakthrough during turndown operations. Additionally, if the TGU Hydrogenation Reactor catalyst is not fully active, then COS and CO conversion tend to fall off first (5).

At turndown, there is significantly higher COS concentration in the Claus tail gas. Even though rates are reduced, meaning more residence time is available in the Hydrogenation Reactor catalyst, if the TGU catalyst is sick, then unconverted COS will slip through the TGU amine system to the Incinerator.

If there is not a TGU downstream of the Claus unit, then stack emissions concentrations directly increase in proportion to the unconverted sulphur. Incineration systems that are permitted on a concentration basis of $SO_2$ in the stack will see an increase in $SO_2$ at turndown, which should be considered at the design stage.

In addition to these points, there are two further complications with turndown operations. The first is the formation of sulphur fog in the sulphur condensers, while the second concerns heat loss. In the case of sulphur fog, conversion to elemental sulphur is not affected directly. It is the recovery of sulphur within the Condensers that suffers. At low mass velocities (< 1 lb/s-ft2), fine droplets of elemental sulphur mist evade capture by conventional mist elimination equipment leading to loss of sulphur recovery efficiency. The risk of reaching the sulphur dew point in a downstream sulphur converter increases, and this is compounded by increased heat loss.

Table 2. Parametric Results from Turndown Case Study

| | 100% of Design 125 LTPD Base Case | 60% of Design 75 LTPD Case 1a | 30% of Design ≈40 LTPD Case 1b |
|---|---|---|---|
| ***Sulphur Throughput (LTPD)*** | 125 | 75 | 40 |
| ***Air Flow (lbmol/hr)*** | 928 | 560 | 302 |
| ***Reaction Furnace Temperature (°F)***[1] | 2390 | 2400 | 2410 |
| ***WHB Peak Tube Wall Temperature (°F)*** | 545 | 530 | 517 |
| ***WHB Peak Heat Flux (Btu/hr·ft²·°F)*** | 36,000 | 26,200 | 18,200 |
| ***WHB Mass Flux (lb/s·ft²)*** | 3.0 | 1.8 | 0.97 |
| ***Sulphur Conversion (%)*** | 96.95 | 96.85 | 96.75 |
| ***Sulphur Recovery (%)*** | 96.46 | 96.43 | 96.33 |
| ***Hydrogen in Tail Gas (mole %)*** | 1.9 | 1.5 | 1.18 |
| ***COS in Tail Gas (ppmv)*** | 319 | 374 | 455 |
| ***$CS_2$ in Tail Gas (ppmv)*** | 0.6 | 0.55 | 0.5 |

1. Simulations ignore heat loss.

Besides the sulphur dew point concerns in the catalyst beds, heat loss reduces the temperature in the Reaction Furnace and is exacerbated at turndown. Wissbaum (6) provided a methodology to estimate heat losses in the Reaction Furnace

Because both the heat loss and sulphur fogging concerns are highly specific to plant configuration, we chose not to explore these facets in this particular work. However, these relative influences are blunted somewhat also by the choice to limit the turndown in a sulphur plant to 30% of design. In the case of a well-designed sulphur condenser, the risk of fogging losses is minimal at 30% hydraulic load.

Table 3 compares the unit operating at 30% turndown on acid gas only versus operating at 30% hydraulic turndown on a mixture of acid gas and natural gas. This latter case is illustrative of an operating point half way through pulling the acid gas out during a shutdown. The Reaction Furnace temperature is a significant concern (+400°F) for both of this case. Here, we limited the temperature by adding tempering steam in the simulation.

Note also from Table 3 that significant changes occur in the WHB and downstream tail gas. The peak heat flux for acid gas alone shows a considerable reduction compared to the full-rate operations. However, when operating on the acid gas plus natural gas mixtures, the peak heat flux shows a much lesser decrease. This can be explained through the much higher Reaction Furnace temperatures for the mixture cases. Because a considerable amount of the combustibles are now hydrocarbon rather than acid gas, the temperature within the furnace is much higher. Tempering steam is needed while combusting significant amounts of hydrocarbons, not only to keep the temperature moderated, but also to mitigate soot formation.

The overall conversion and recovery is quite considerably reduced under the startup/shutdown operations compared to both the full rate, and even vs. 30% turndown on acid gas only. If the operating company is mandated to meet a certain percent recovery or $SO_2$ concentration in the stack, this could very plausibly prevent the plant from meeting the permitting requirement.

Table 3. Parametric Results from 50% Startup/Shutdown Case Study

| | Base Case | ≈30% of Design Acid Gas Only Case 1b | ≈30% of Design 50:50 Acid Gas with: Natural Gas Case 2 |
|---|---|---|---|
| ***Sulphur Throughput (TPD)*** | 125 | 40 | 20 |
| ***Air Flow (lbmol/hr)*** | 928 | 302 | 341 |
| ***Reaction Furnace Temperature (°F)***[1] | 2390 | 2410 | 2815 |
| ***WHB Peak Tube Wall Temperature (°F)*** | 545 | 517 | 530 |
| ***WHB Peak Heat Flux (Btu/hr·ft²·°F)*** | 36,000 | 18,200 | 26,200 |
| ***WHB Mass Flux (lb/s·ft²)*** | 3 | 0.97 | 0.865 |
| ***Conversion (%)*** | 96.95 | 96.75 | 91.29 |
| ***Recovery (%)*** | 96.46 | 96.33 | 89.65 |
| ***Hydrogen in Tail Gas (mole %)*** | 1.9 | 1.18 | 4.6 |
| ***COS in Tail Gas (ppmv)*** | 319 | 455 | 720 |
| ***$CS_2$ in Tail Gas (ppmv)*** | 0.6 | 0.5 | 0.4 |

1. Simulations ignore heat loss.

## Conclusions

Although startup and shutdown procedures are short term actions in any sulphur processing facility, there are long term implications if not properly considered integrally, both within the design phase, as well as during operations. Careful measures need to be taken to avoid damaging the integrity of the unit, which will cause untimely repairs to be required. Utilizing the kinetic and heat transfer rate-based sulphur simulator, SulphurPro™, will help give much better understanding of the operations during these procedures, allowing steps to be taken to plan for and mitigate potentially costly events revealed by the simulations.

Turndown also needs to be carefully monitored and given ample consideration right from the start. Knowing the limitations of the unit and what may occur during these turndown operations will help prevent unnecessary repairs and downtime. Design targets can additionally be set more intelligently using the rate based kinetics in SulphurPro.

## References

1. “Factors Affecting Claus Waste Heat Boiler Design and Operations”, Elmo Nasato, Nathan Hatcher, Simon Weiland and Steven Fluk, Sulphur 2018
2. “Examining the Impact of Waste Heat Boiler Design and Operation on WHB Reliability”, Elmo Nasato, Domenica Misale-Lyttle, David Barrow and Michael Huffmaster, Sulphur 2015.
3. “Evaluate waste heat steam generators”, W.P. Knight, Hydrocarbon Processing. 1978.
4. “Design Considerations for Modified Claus Sulphur Recovery Plants”, B. Gene Goar, Proceedings of the Comprimo/Western Research Seminar on Gas Sweetening and Sulphur Recovery, November 1985, Amsterdam, The Netherlands
5. “Low Temperature Tail Gas Kinetic Functions – What They Are – Really”, Karl Krueger, Fernando Maldonado, Michael Huffmaster, Brimstone Conference Proceedings 2016
6. “How Hot is Your Reaction Furnace – Really?”, Blais, D., Marshall, C., Wissbaum, D., Proceedings of the 2012 Laurance Reid Gas Conditioning Conference, February 2012, Norman, OK.