

“SRU Shutdowns and Startups with Fewer Emissions and Shorter Duration”

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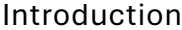
ABSTRACT

Sulfur Recovery Units (SRUs) face increasing SO₂ emissions reduction challenges during shutdown and startup. The development of new procedures and best practices is necessary to efficiently prepare the plant for safe entry and condition catalyst for normal operation. This paper provides an overview of the methodologies and benefits of adopting best practices for shutdown and startup procedures that not only minimize emissions but reduce the overall downtime to allow a quicker return to service for supporting refinery operations.

Topics include:

- Streamlined shutdown procedures
- Elimination of excess SO₂ emissions during passivation
- Catalyst activation and feed introduction in less than a day

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As the global energy sector intensifies its focus on sustainability and operational excellence, sulfur recovery units (SRUs) remain critical to both environmental compliance and refinery profitability. Try operating a refinery Coker without any SRUs!

While much attention has been given to optimizing steady-state operations to support Cokers and FCCs, the shutdown and startup steps—particularly for planned turnaround maintenance—present a unique merging of safety, environmental, and economic challenges.

A properly executed SRU shutdown is essential to ensure safe entry for operations and maintenance personnel. This includes sulfur-freeing the equipment, passivating pyrophorics, and a controlled cool down to prevent injury or equipment damage. However, these steps, if not carefully managed, can result in significant sulfur dioxide (SO₂) and other emissions, often exceeding those generated during normal operations. At the same time, extended shutdown durations can constrain upstream production, disrupt customer supplies, and erode margins.

To address these competing priorities, it is imperative to develop and adopt best practices that minimize emissions while at the same time reducing downtime. Through capturing lessons learned, new procedure test runs, and sharing of continuous improvements, SRUs can accelerate the development of shutdown protocols that are both environmentally responsible and operationally efficient.

Ultimately, the goal is to return the SRU to service in a condition that supports longer, more reliable run lengths—delivering sustained compliance, improved safety, and uninterrupted production.

Regulatory Landscape: Emissions Requirements and Regional Variability

The emissions profile of an SRU during shutdown is subject to a complex and evolving regulatory framework that varies significantly across jurisdictions. While federal standards provide a baseline, local permitting authorities often impose additional requirements that reflect regional environmental priorities and air quality goals.

At the federal level, the U.S. Environmental Protection Agency (EPA) establishes National Emission Standards for Hazardous Air Pollutants (NESHAP) for petroleum refineries. For sulfur recovery units, some jurisdictions require that emissions during startup, shutdown, and maintenance events must either meet the same limits as normal operations or comply with alternative work practice standards if those limits cannot be achieved.

However, the application of these standards is not uniform. In some air districts—particularly those with historically poor air quality or aggressive climate action plans—permits require that SRUs meet normal operating emission limits even during shutdowns. For example, some facilities in California Districts may be held to stricter thresholds, with limited or no allowance for elevated emissions during transient events. These local rules often require detailed shutdown protocols, increased monitoring, and in some cases additional treating equipment.

Sources of Emissions During SRU Shutdown

Sulfur recovery unit shutdowns are inherently complex and, if not carefully managed, can result in significant SO₂ emissions. Understanding the primary sources of these emissions is essential for developing effective mitigation strategies that align with both safety and environmental performance goals.

The most critical emissions-generating step during shutdown is the passivation process, which is required to safely oxidize pyrophoric materials—primarily iron sulfide (FeS)—that accumulate in reactors and sulfur-handling equipment. These pyrophoric materials present a significant risk of fire and containment loss if subjected to excessive air exposure during operational or maintenance activities. To neutralize them, oxygen from air is introduced in a slow and controlled manner, converting FeS to iron oxide and generating SO₂ and heat in the process.

Prior to the passivation step, the sulfur melt-out step, which can be an equally important step, is necessary to remove residual molten sulfur from the thermal reactor, catalyst, condensers, and process piping. If this step is rushed, incomplete, or skipped, residual sulfur can become a fuel source during subsequent air passivation steps, leading to uncontrolled burns or fires and excessive SO₂ emissions.

Historically, shutdown procedures were designed to melt out and passivate the Claus section while bypassing the tail gas treating unit (TGTU). This approach allowed the Claus and TGTU sections to be passivated in parallel when emission limits were less stringent, which usually resulted in reduced shutdown time. Because the TGTU was not in service to treat the SO₂ generated during Claus passivation, the emissions were vented directly to the thermal oxidizer, bypassing a potential treating step. This practice often resulted in exceedances of permitted emission limits and increased environmental risk. With the increasing pressure to minimize emissions, additional time was required to slowly passivate in order to maintain the rolling hourly emissions below permitted limits.

New best practices and procedures now emphasize a more “normal operation” approach, where the TGTU remains online during Claus passivation to capture and treat SO₂ for as long as possible. This sequencing aims to minimize emissions while executing safe and efficient shutdown procedures. However, implementing these improvements requires careful planning, increased monitoring, and additional equipment procedures.

Some discussion about burners is necessary; this covers the thermal reactor, auxiliary reheater, and reducing gas generator (RGG) burners. Managing excess oxygen is important for controlling pyrophoric passivation, so the operation and condition of burners must be evaluated. Legacy burners with limited turndown usually experience some damage from backburning throughout the run. Even after reconditioning and steam or nitrogen injection, mixing can remain insufficient, making excess oxygen control more challenging. When these burners are damaged, both soot detection and excess oxygen presence are possible. Therefore, auxiliary reheat burner use is restricted to the minimum required. The use of a single oxygen source—the thermal reactor burner—is recommended for the Claus section. If steam reheaters are available, they eliminate the risk of oxygen leakage and should be used when advantageous.

In summary, the dominant contributors to SO₂ emissions during SRU shutdowns are:

1. Incomplete sulfur melt-out, which can result in residual sulfur reacting with oxygen during subsequent passivation steps.
2. Passivation of pyrophorics, which must be carefully controlled to avoid thermal excursions and excessive oxidation.
3. Bypassing the TGTU during Claus passivation, a legacy practice that increases emissions by removing the final treatment step from the shutdown sequence.

By understanding and addressing these sources, operators can significantly reduce emissions, improve safety, and support a faster return to reliable operation.

Evolving Best Practices: Sequential Passivation Through the TGTU Reactor

To address the limitations of legacy shutdown procedures and reduce SO₂ emissions, a new best practice and procedure was developed: conducting the melt-out and passivation of the Claus section through the TGTU in series. This approach contrasts with older methods that bypassed the TGTU during Claus passivation, allowing both sections to be passivated in parallel but at the cost of longer durations and higher emissions.

In this updated procedure, the Claus section is first melted out and passivated while maintaining flow through the TGTU reactor. This sequencing ensures that SO₂ generated during Claus passivation is routed through the hydrogenation reactor, where it is catalytically reduced to hydrogen sulfide (H₂S) and then absorbed in the amine system as during normal operation—significantly reducing atmospheric emissions.

Once the Claus section is mostly passivated and there is oxygen breakthrough, the TGTU reactor itself is passivated using a carefully controlled oxygen introduction strategy from only the thermal reactor. Passivation best practices highlight the importance of maintaining all reactor temperatures below 700°F to avoid catalyst, reactor grid, process piping or refractory damage, while gradually increasing oxygen concentrations into the TGTU to oxidize residual pyrophorics and eventually Co / Mo sulfides.

A significant improvement in this procedure involves the integration of the quench column downstream of the TGTU reactor, which functions as an SO₂ scrubber. This system effectively removes residual SO₂ from the gas stream during the final hours of both Claus and TGTU passivation phases, thereby further minimizing emissions before directing the stream to the thermal oxidizer.

The inclusion of the SO₂ scrubber facilitates quicker passivation by reducing the need for prolonged passivations required to comply with rolling hourly average emission limits. Additionally, it enables a more controlled and predictable shutdown process, aiming to decrease downtime and ensure continuity in production.

Quench Column Chemistry: Managing SO₂, CO₂, and Material Integrity

The quench column is a critical emissions control component during SRU shutdowns, operated to scrub SO₂ from the process gas using a caustic solution, a different purpose than in normal operation. The chemistry involved is rapid and highly effective—provided that pH is carefully maintained within a narrow optimal range.

SO₂ Neutralization Reactions

Once SO₂ is absorbed into the aqueous phase, it reacts with NaOH in two primary pathways:

- $\text{SO}_2 (\text{v}) + \text{NaOH} (\text{l}) \rightarrow \text{NaHSO}_3$ (sodium bisulfite)
- $\text{SO}_2 (\text{v}) + 2\text{NaOH} (\text{l}) \rightarrow \text{Na}_2\text{SO}_3$ (sodium sulfite) + H_2O

The dominant reaction depends on the pH of the solution:

- At pH 6.0–7.0, the system favors the formation of sodium sulfite (Na_2SO_3), which accounts for 90–98% of the reaction products.
- Only 2–10% of the products are sodium bisulfite (NaHSO_3) in this range.

This pH window is ideal for maximizing SO_2 capture while minimizing corrosivity.

CO_2 Interference at High pH

If the pH exceeds 7, carbon dioxide (CO_2) in the gas stream begins to interfere with SO_2 scrubbing by reacting with NaOH to form:

- $\text{CO}_2 + \text{NaOH} \rightarrow \text{NaHCO}_3$ (sodium bicarbonate)
- $\text{CO}_2 + 2\text{NaOH} \rightarrow \text{Na}_2\text{CO}_3$ (sodium carbonate) + H_2O

These reactions consume caustic that would otherwise be available for SO_2 neutralization, reducing scrubbing efficiency and increasing neutralizer usage. Additionally, carbonate formation can lead to scaling and fouling in equipment.

Corrosion Risk at Low pH

If the pH drops below 5, the environment in the quench column becomes increasingly acidic, which poses a significant risk to carbon steel materials commonly used in its construction. Under these acidic conditions, iron in the carbon steel reacts with acidic species, leading to accelerated corrosion. Over time, this can result in pitting, thinning, and eventual failure of piping, pumps, and other high-velocity components within the system.

To prevent material degradation and ensure long-term equipment integrity, it is essential to maintain the quench column pH above 5. If pH drops below 5, immediate corrective action—such as controlled caustic addition—is required to restore neutral conditions and protect carbon steel surfaces.

6. Maintain Claus section coupled to TGTU
 - a. Melt-out and passivation through the TGTU reactor
 - b. Maintain flow through amine absorber as long as possible
 - c. Leave air demand analyzer in service for SO₂ indication
7. Hold at melt-out conditions with slightly excess O₂
 - a. Continue until condensers stop draining to ensure sulfur removal
 - b. Conduct frequent checks for sooting
 - c. Conduct frequent excess oxygen checks with portable meters
8. Check condenser rundown lines for plugging
 - a. Especially important for historically problematic units before increasing air
 - b. Ensure condensers are not sulfur packed from rundown plugging
9. Begin passivation sequence
 - a. Gradually raise air to thermal reactor burner to passivate:
 - b. TRX → Claus reactors → TGTU reactor → Quench column → Thermal oxidizer
10. Control reactor bed temperatures
 - a. Do not exceed 700°F during passivation in any reactor
11. Passivate Claus and TGTU reactors in series
 - a. Use quench column with caustic buffering to minimize SO₂ emissions
 - b. Load the quench column with 2 wt% caustic solution for SO₂ scrubbing
 - c. pH drop will be indication of SO₂ breakthrough
 - d. Maintain pH between 6-7
12. Hydrogenation reactor temperature
 - a. SO₂ breakthrough is an indication hydrogenation reactor is passivating and amine absorber should be removed from service
 - b. Reduce reactor inlet temperature to lower bed temperatures, as needed
 - c. If CEMS SO₂ > 250ppm then reduce excess oxygen at thermal reactor outlet

13. Monitor SO₂ breakthrough at quench column

- a. ~100 ppm at pH 6
- b. ~4 ppm at pH 7
- c. Add caustic if pH drops below 5; do not exceed pH 7

14. Adjust combustion air if emissions exceed limits

- a. If SO₂ emissions are high and caustic spending too fast reduce air to thermal reactor burner

15. Monitor thermal reactor flame stability

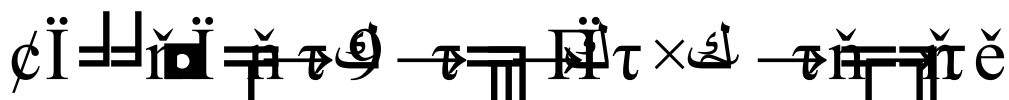
- a. Expect eventual flame-out as air/fuel ratio increases
- b. Ensure isolation of moderating steam before flame-out

16. Confirm passivation completion when:

- a. Excess O₂ >10-20% at Claus and TGTU reactor inlets, and
- b. No reactor exotherms with increased air

17. Begin cooldown

- a. Ramp down thermal reactor temperature at a controlled rate of 100°F/hr



Preparation and Pre-Passivation Steps

1. Complete Sulfur Removal (Heat Soak & Melt-out): Before introducing any excess air, ensure all acid gas feed to the Claus unit is stopped and perform the standard heat soak and sulfur melt-out steps to remove the bulk of elemental sulfur from reactors and condensers. This involves maintaining high reactor temperatures ($\approx 260^{\circ}\text{C}/500^{\circ}\text{F}$) with stoichiometric fuel firing to melt and drain out sulfur from catalyst pores and equipment. Continue melt-out until sulfur flow from all condensers has ceased. Rationale: Removing as much sulfur as possible in this stage minimizes fuel for unwanted fires when oxygen is later introduced.
2. Line Up Sulfur Thermal Oxidizer/Treatment: Ensure the tail gas from the SRU is properly routed to the thermal oxidizer and that the TGTU remains in service during the initial Claus passivation. This allows any SO_2 formed during passivation to be treated and prevents unprocessed $\text{H}_2\text{S}/\text{SO}_2$ releases. Confirm the thermal oxidizer (or TGTU absorber) is online and that SO_2 measurements from the air demand analyzer and stack CEMS are available. Functioning portable O_2 analyzer availability should be confirmed.
3. Personnel and Equipment Safety Checks: Clear non-essential personnel from the area and establish barriers as needed. Ensure work permit controls and personal protective equipment (PPE) are in place due to the potential for SO_2 gas and hot surfaces. All burner viewports should be clean for monitoring flames, and emergency escape routes should be free of obstructions.
4. Temperature Stabilization: Verify that Claus reactor bed temperatures are at the recommended levels for passivation. Ideally, allow the reactors to start cooling after melt-out: each catalyst bed inlet should be around 160°C (320°F) before introducing significant oxygen. The TGTU quench tower and circulating coolers should be operating to lower gas temperatures. Do not exceed a cooling rate of $\sim 50^{\circ}\text{F}$ per hour on reactor beds to avoid thermal stress. Do not exceed $\sim 50^{\circ}\text{F}$ per hour cooldown on the WHB shell side to avoid mechanical and thermal stress.

Controlled Passivation of Claus Unit Reactors

After sulfur removal, the Claus catalytic reactors must be oxidized in a controlled manner to neutralize pyrophorics:

5. **Ensure Adequate Flow:** To achieve effective passivation of pyrophorics within the Claus reactors, it is essential to maintain a minimum volumetric flow rate of at least 25% of the unit's design capacity. Adequate flow ensures uniform distribution of air and reactant gases throughout all catalyst beds, preventing localized stagnation and incomplete oxidation. This helps guarantee that all surfaces and pockets of pyrophoric material are thoroughly contacted by oxidizing gases, reducing the risk of subsequent hotspots or uncontrolled reactions during or after passivation.
6. **Gradually Increase Air at Thermal Reactor Burner:** In the Claus thermal stage burner, begin increasing the air-to-fuel combustion ratio to introduce a slight excess of oxygen into the system. Adjust the air flow upward in small increments – raise the air flow setpoint to achieve about 0.1%–0.5% O₂ in the WHB effluent (usually 10:1 mole ratio). Hold each adjustment for a monitoring period (e.g. 15–30 minutes) and observe reactions. To confirm good excess oxygen control, monitor tail gas SO₂ from air demand analyzer < 0.5% vol during this phase – a large SO₂ spike indicates too rapid oxidation in the Claus section. Use the tail gas analyzer and an oxygen analyzer at the WHB outlet to guide you. Key point: At this stage, oxygen is kept very low (less than 1%) to prevent a rapid combustion of residual sulfur while initiating FeS oxidation.
7. **Monitor Bed Temperatures and SO₂ Closely:** Continuously watch each Claus converter bed's temperature indicators. A slow rise in bed temperatures is expected as FeS and residual sulfur oxidizes. If any bed's temperature starts to rapidly increase or approaches 370°C (700°F), take immediate action: reduce the oxygen by cutting back air or adding more fuel to consume excess O₂. In case of a sharp exotherm ("sulfur fire"), temporarily reverting back to purely stoichiometric conditions must be made to quench the reaction. It's critical that bed temperatures remain controlled; ideally keep them < 315°C (600°F) during most of the passivation. Also observe the thermal oxidizer stack SO₂ – a sudden rise indicates a rapid burn in the reactors. Every 30 minutes, sample the thermal stage effluent with a portable O₂ analyzer to verify excess O₂ levels are in target range. Again, utilize the SO₂ reading from the air demand analyzer to help manage excess oxygen.
8. **Incrementally Increase Excess Air:** If temperatures are stable, continue to raise the excess O₂ in small steps. For example, increase the air ratio by a few percent at a time. Each time, wait and ensure:
 - O₂ slip (at the thermal reactor outlet or upstream of the first converter) stays in the low percentage range (e.g. 1–2% vol initially).

- Converter bed temperatures do not climb uncontrollably (a gentle rise and then fall-off indicates pyrophoric oxidation is occurring and then subsiding).
- Soot is not occurring (perform a “white paper test” on thermal reactor WHB outlet gas if possible – no soot deposition should be seen).
- SO₂ at final sulfur condenser outlet remains manageable (e.g. <0.5% vol as a guideline).

Over a period of hours, as the catalyst beds become oxidized and cool further, you can allow more O₂. Aim to reach about 10% vol O₂ in the thermal reactor effluent gas by the end of Claus passivation; ensure to close and isolate flame moderation steam. By this point, the majority of iron sulfides in the Claus beds will have converted to iron oxide, and any residual sulfur will have reacted to SO₂.

Note: A successful Claus passivation is indicated when all reactor bed thermocouples show <163°C (325°F) while O₂ breakthrough exceeds ~10% without further temperature hikes. This means the beds are fully “passivated” and no fuel for exothermic reaction remains. Continue blowing combustion air through the system at this stage to further cool the reactors.

9. Full Air Sweep and Cool Down (Claus Section): Once passivation is achieved, you can stop any fuel firing to the thermal reactor burner entirely and allow the main combustion air blower to push ambient air through all Claus reactors. This will further oxidize any last traces of sulfide and help cool the equipment. Maintain a maximum average cooldown rate (~100°F per hour) by keeping all air on and using any available cooling (air, nitrogen, or draining condenser BFW). At this point, the Claus reactors are fully passivated and ready for opening. All sulfur and FeS should be inert, evidenced by stable low temperatures and oxygen in the effluent essentially equal to atmospheric (~21% O₂) without SO₂ or other reaction products.

Controlled Passivation of TGTU Catalyst

The TGTU catalyst operates in a sulfided state and will also have pyrophoric iron sulfide on its surfaces. However, passivating the TGTU requires special care to avoid damaging the catalyst and equipment since this hydrogenation catalyst contains Cobalt and Molybdenum metals.

10. Isolated or Coupled to Claus Section: The TGTU catalyst may be passivated in series with the Claus section or isolated for passivation in parallel. If passivated in parallel, the isolated TGTU tail gas is already going to the thermal oxidizer. The TGTU should be put on internal circulation. Block in the inlet and outlet of the TGTU

(except for a small vent to the thermal oxidizer) and establish a recirculation loop using the TGTU's recycle gas blower or an auxiliary ejector ensuring the rate is at least 25% of the design. This creates a closed loop through the hydrogenation reactor and quench tower. Maintain a slight positive pressure (for example, ~1–5 psig) in the loop to assist circulation.

11. Purge Reducing Gas and Cool the TGTU Reactor: Ensure that any residual hydrogen or reducing gas is purged from the TGTU system. Gradually cool down the TGTU catalyst bed. Lower the RGG outlet temperature and use the quench system to lower reactor temperatures. Ensure the steam to fuel rate is at least 4 : 1 mass ratio. Aim to bring all the reactor bed temperature indicators to 200°C (400°F) before admitting oxygen. Do not introduce air while the TGTU catalyst is hot; the catalyst's active metal sulfides can rapidly oxidize leading to catalyst and equipment damage. Also, too low passivation temperature may not fully initiate oxidation reactions...a delicate balance.
12. Initiate Low Rate Air Injection into TGTU Loop: Once the TGTU reactor is cooled and the loop contains essentially combustion gases, begin introducing air at a very low rate into the circulating gas. There may be a dedicated air injection passivation valve, or you can slightly increase the air/fuel ratio. Target an initial oxygen concentration of only about 0.5%–1.0% vol O₂ in the RGG outlet. A mild temperature rise (a few °F) across the bed indicates oxidation of pyrophorics has started. Hold this low O₂ level until temperatures stabilize.
13. Stepwise Oxidation in TGTU Reactor: Continue the passivation in increments:
 - If the initial air addition caused little to no exotherm (e.g., reactor bed temperatures rose only a few degrees and then leveled off), you can slightly increase the O₂ concentration. Raise it to ~2%–3% O₂ and continue close monitoring for the next 30 minutes.
 - Repeat the cycle: watch for temperature increases, wait for them to peak and begin falling, then bump the O₂ a bit higher. Do not rush this process – the oxidation in the TGTU catalyst may occur in stages. By waiting ~30 minutes or more at each step, you allow the exothermic reactions to subside and avoid stacking temperature deltas.
 - Monitor the temperature delta across the reactor (bed inlet vs. outlet). A noticeable rise indicates active oxidation. If at any point a temperature approaches 315°C (600°F), stop air rate increases.

- If any bed's temperature starts to rapidly increase or approaches 370°C (700°F), take immediate action: reduce the oxygen by cutting back air or adding more fuel to consume excess O₂ and return to stoichiometric firing.
- Continue increasing the O₂ stepwise in 1% increments up to about 5%, then 10% vol. It may take a couple of hours to reach ~10% O₂, depending on how much FeS is present.

The end goal is that the reactor can have ~15–20% O₂ in the gas without any significant temperature rise, meaning the pyrophoric material has been largely consumed. At that point, the TGTU catalyst's cobalt/molybdenum sulfides are converted to the oxide phase.

14. Purge and Cool the TGTU for Opening: When satisfied that no further oxidation is occurring, move to the cooling step. Continue to circulate through the reactor to cool it down. Cool the reactor to near-ambient temperature.

Post-Passivation Verification and Equipment Opening (Claus and TGTU Catalyst Beds)

15. Safety Verification Before Opening: Before any equipment handover for mechanical opening, perform a thorough check:

- Temperature Check: Verify via DCS thermocouples that all catalyst beds, vessels, and piping indicators are at or near, at most, the combustion air blower outlet temperature. No hot spots should remain in any catalyst bed or equipment.
- Gas Testing: Use portable instruments to sample the vapor space of the reactors (through bleed valves or analyzer points) for oxygen, H₂S, and SO₂. Ideally, you should find oxygen present (from the air purge) and little to no H₂S. A small residual SO₂ reading is possible, but it should be very low (only trace ppm). If significant H₂S is detected, initiate purging with air until tests are clear.
- Oxygen Level: Ensure O₂ is not completely depleted in the vessel – you want some O₂ so that if any last FeS is exposed it won't find a fresh air surge unexpectedly.

16. Equipment Entry and Handling of Catalyst: With the vessels open, keep them ventilated (natural draft or with air movers) while work is ongoing. The catalysts, now passivated, should not reignite upon air contact, but avoid disturbing large volumes of catalyst until it's confirmed cool and passivated throughout. Often, a light water mist can be sprayed on catalyst surface once opened, as an added

measure to prevent dust and cool any smoldering spots. Continuous confined space monitoring should include at a minimum H₂S and SO₂.

By following the above procedure, the Claus and Tail Gas unit catalysts and equipment will have been safely passivated with excess air, meaning all pyrophoric materials have been oxidized under controlled conditions. The equipment can now be opened to the atmosphere and worked on without risk of fire or uncontrolled toxic gas release. Always adhere to site-specific safety rules and obtain proper work permits for vessel entry. This method ensures a safe shutdown, protecting both personnel and equipment, while preserving catalyst for future use if applicable.

Table: Key Passivation Parameters and Safety Thresholds

Parameter	Target During Passivation	Rationale / Notes
Excess O ₂ (Claus)	0.1–0.5% vol initially on portable; up to ~10% vol in final stages	Tightly limit O ₂ slip early to prevent sulfur fires; gradually increase once sulfur is removed and FeS oxidation is under control.
Tail Gas ADA SO ₂ level	< 0.5% vol during Claus passivation	Continuous indicator of controlled burn rate. Elevated SO ₂ means too much O ₂ or a sulfur exotherm in progress, requiring adjustment.
Claus Bed Temps	Keep < 160°C (325°F) during O ₂ introduction	Provide plenty of buffer below catalyst maximum temperatures during passivation.
TGTU Catalyst Temp	Target 200°C (400°F) before adding O ₂	Minimum required temperature to initiate Co/Mo catalyst oxidation. Low temperature limits exotherm intensity.

Parameter	Target During Passivation	Rationale / Notes
TGTU O ₂ Concentration	Start ~0.5%–1% vol; stepwise to ~10%+	Low O ₂ ensures gentle FeS oxidation.

pH is not maintained on the alkaline side, the solution can become strongly acidic. Carbon steel, which is commonly used for quench column shells, piping, and internals, corrodes at $\text{pH} < 5$ in sour water.

Preventing Corrosion: The key to mitigating corrosion risk is always maintaining quench water pH in a safe range. Operating guidance is to keep pH around 6–7 and certainly prevent it from dropping below 5.0. Caustic addition is used to neutralize incoming SO_2 and hold the pH up. However, over-shooting to very high pH is also discouraged. Thus, tight pH control is essential: enough NaOH to neutralize acids, but not so much as to start picking up CO_2 .

Wastewater Effluent Concerns: The scrubbing process generates spent caustic solution containing dissolved sodium sulfite (Na_2SO_3), sodium bisulfite (NaHSO_3), sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) and possibly sodium sulfate (Na_2SO_4). This solution typically circulates in the quench loop during the procedure. This sour water, either as a continuous purge or when passivation is complete, will need to be disposed of or treated. Common practice is to route it to the refinery's wastewater treatment system.

Key environmental considerations for this liquid stream include:

- **pH and Neutralization:** The spent scrubbing solution can be highly alkaline (especially if excess NaOH remains) or somewhat neutral if most NaOH was consumed. It often requires neutralization to $\text{pH} \sim 7$ before final discharge. Many refineries neutralize process water automatically in their water treatment plant.
- **Sulfite Oxidation:** Sulfite (SO_3^{2-}) in water will oxidize to sulfate over time, consuming oxygen. A high load of sulfite in a wastewater plant can deplete dissolved oxygen and upset biological treatment. However, some of the sulfite from scrubbing will convert to sulfate in the quench itself due to air from the passivation. Still, the wastewater treatment area must watch for chemical oxygen demand (COD) spikes due to sulfites/thiosulfates in the water outfall.

Risk Mitigation and Best Practices

To successfully use a quench column for SO_2 removal during Claus unit passivation, the following best practices and considerations are put forward to mitigate the identified risks:

- **Thorough Procedure and Training:** Develop a detailed shutdown procedure that includes using the quench as an SO_2 scrubber. Spell out steps for caustic addition, pH monitoring, and contingency actions. Train operators on the scrubbing chemistry and consequences of pH excursions.

- **Pre-Charge and Pre-Check the Quench System:** Before introducing O_2 for passivation, pre-charge the quench circulation with caustic to achieve an initial pH in the target range. For example, add enough NaOH to get ~1–3 wt% in the water, then recirculate to mix evenly. Ensure the pH probe is calibrated and reading accurately at alkaline pH. Verify the quench circulation rate is at max design and that the pump is in good working order. Clean or replace quench loop filters in advance so they start fresh.
- **Management of pH:** Set a pH range 6-7 during the bulk of passivation; this gives some buffer so if a slug of acid comes, it drops into the 6s but not below 5 before an adjustment is made.
- **Maintain Reducing Conditions Until Ready:** One strategy to reduce SO_2 scrubbing is to keep the TGTU hydrogenation reactor in reducing mode as long as possible. For instance, do not cut the fuel to the RGG too early – you want residual H_2 in the gas to convert some SO_2 back to H_2S in the catalyst bed initially, which the amine system can treat. Only once the Claus beds are largely passivated (and sulfur burned off) should you allow O_2 to break through to the TGTU reactor. At that point you focus on scrubbing. This sequencing can minimize the total SO_2 that needs scrubbing.
- **Isolate or Protect the Amine System:** Ensure the amine absorber is drained or bypassed so that SO_2 does not enter the circulating amine. If SO_2 were to reach amine, it would form heat stable salts that could permanently damage the amine.

Chemistry of Caustic Scrubbing in a Quench Column (CO_2 vs. SO_2 Dynamics)

During Claus unit passivation, introducing air generates significant SO_2 in the tail gas, which is cooled and scrubbed in the TGTU quench column using a caustic (NaOH) solution. However, this tail gas also contains a high concentration of CO_2 (from natural gas combustion), raising concern that excess NaOH could be wasted reacting with CO_2 instead of capturing SO_2 .

One mole of CO_2 consumes 1 mole of NaOH to yield sodium bicarbonate. This typically occurs when solution pH is moderately alkaline (around 7–9). With excess NaOH (pH well above 10), CO_2 will be fully converted to sodium carbonate - this uses 2 NaOH per mole of CO_2 . Any CO_2 captured will effectively “steal” NaOH at up to 2:1 ratio, yielding carbonate waste that does not contribute to SO_2 removal. This underscores why we want to fine-tune caustic addition: to use just enough base to neutralize SO_2 , but not so much that we start soaking up large amounts of CO_2 . In practical terms, SO_2 will dissolve and react even in near-neutral water, while CO_2 needs a high-pH environment to continue absorbing.

Impact of CO₂ on SO₂ Scrubbing Efficiency

A high CO₂ content in the tail gas can potentially divert caustic away from SO₂ if the scrubber is not well-controlled. Claus tail gas during passivation might contain CO₂ on the order of 10–15% or more by volume (from combustion of fuel), whereas SO₂ concentration might be at most a few percent. Thus, in raw quantity terms, CO₂ is present in an order of magnitude higher amount than SO₂. If the caustic scrubber were run at very high pH (excess NaOH), it would indiscriminately absorb both gases: CO₂ being 10× concentration of SO₂ means it could consume a large fraction of the NaOH.

However, because CO₂ is relatively weakly absorbed at moderate pH, a properly operated scrubber can selectively remove SO₂ with minimal CO₂ uptake. Key points:

- SO₂ is much more soluble and reactive in the scrubbing solution than CO₂ at the same pH. At low pH (acidic solution), CO₂ stays in gas (it won't dissolve because the water lacks free OH⁻ to neutralize it), whereas SO₂ still dissolves significantly (forming H₂SO₃ which ionizes to HSO₃⁻). This means the presence of abundant CO₂ “should not pose much of a problem” if the scrubber is run such that the pH is on the lower end of the alkaline range.
- CO₂ absorption threshold: Industry experience confirms that if you maintain the quench liquid pH in the neutral to slightly alkaline range (say 6-7), CO₂ slip remains high (which is desired – it means CO₂ passes through to the thermal oxidizer instead of reacting). An SO₂ absorber often operates with effluent water pH around 5–7, precisely to avoid excess CO₂ pickup. In contrast, SO₂ removal can still be achieved even as the solution becomes mildly acidic.
- Effect on SO₂ removal: Running at such lower pH does slightly reduce SO₂ capture efficiency because less free NaOH is present. If pH drops too low (<~4), SO₂ starts to break through (the liquid can't neutralize it fast enough). So there is an optimal window: pH as low as feasible to deter CO₂, yet high enough to meet SO₂ outlet specs.
- Consequences of too high pH: If someone mistakenly kept, say, pH 10 in the quench, the outcome would be:
 - Virtually all SO₂ captured (good) – but it would all form sulfite (Na₂SO₃).
 - A significant portion of CO₂ captured as bicarbonate/carbonate. At pH 10, CO₂ absorption is moderate; at pH 11+, it's strong. At 10, perhaps a portion of CO₂ still slips, but a lot will dissolve until the solution capacity is reached. This would

likely more than double the NaOH usage per unit SO₂ removed and produce a spent solution rich in Na₂CO₃.



Introduction

Startup of a Sulfur Recovery Unit (SRU) and its Tail Gas Treatment Unit (TGTU) is a delicate operation that must be done methodically to ensure safety, protect equipment, and achieve efficient sulfur recovery. Operating conditions during startup are far from steady-state – thermal stresses and transient conditions can be more damaging to equipment than years of normal operation. While the return to normal operation is often pressured to take place as expediently as possible, experience shows that rushing or skipping essential steps to save time often can result in equipment or catalyst damage, possibly necessitating another outage.

Key steps and considerations for a safe, controlled startup of an SRU and TGTU start with the detail-engineered Burner Management System (BMS) light-off sequence and SIS validation steps. These critical validations are followed by light-off of the thermal reactor on natural gas then controlled refractory heat-up (~100°F/hour average ramp rate). In parallel there must be a controlled WHB shellside heat-up (~25°F/hr) to avoid mechanical and thermal shock of the high-pressure boiler. Conventional Claus startup guidance has included minimum thermal reactor and converter bed temperature requirements for acid gas feed introduction. While usually there is more than enough time to have established minimum temperature limits in the Claus converters, there are startup cases where this can be the limiting time constraint and prolong the startup procedure. After establishing stable thermal reactor and converter operation, startup guidance often also requires steps to sulfide (activate) the cobalt/molybdenum catalyst in the TGTU's reactor before introducing acid gas feed to the front end of the SRU. The sulfiding procedure has historically proven to be time consuming, risk catalyst damage, result in excess emissions, and prolong acid gas feed introduction.

Development and adoption of new best practices that challenge the status quo with regard to some of these conventional startup practices have proven to effectively reduce overall startup time of the SRU and TGTU while reducing risk to equipment, maintaining emissions compliance, and ensuring a safe and reliable return to normal operation.

Controlled Thermal Reactor Heatup

The thermal reactor design includes a refractory lining system including refractory hot-face bricks which are high-density, heat-resistant ceramic blocks (often high-alumina or chromia) that protect the steel shell from high temperatures and chemical attack. The refractory is vulnerable to spalling, which refers to pieces of refractory breaking off, often caused by thermal stress. Sudden heating or cooling creates steep temperature gradients between the brick hot face and its cooler interior, causing differential expansion that can crack the brick.

Proper heat-up procedures and thermocouple monitoring aim to mitigate these stresses. The API Std 565 recommendation is to not exceed 200°F/hr heatup rate for previously dried out refractory linings [3], while many operators use 100 °F/hour as a target average heat-up rate once dry-out is complete. This allows the bricks' temperature gradient to equilibrate, minimizing thermal shock. It is also recommended to limit the WHB shellside heat-up at a rate less than 25°F/hr to avoid mechanical and thermal shock of the high pressure boiler. Some sites have a shellside temperature indicator that can be used for monitoring this while others can calculate the saturated steam temperature as a function of shellside pressure through the heatup.

With advancements in pilot burners, high intensity ignitors, and burner technology (particularly for higher turndown), the ability to control thermal reactor heatup rates should be more readily achievable now than it was with older equipment. In addition, the modern Burner Management System (BMS) infrastructure allows for automating repeatable, safe and controlled startups as needed to facilitate the heatup process. While many SRU operators employ temporary burners installed specifically for the difficult to manage low-temperature dryout stage, implementing new operating procedures with operational discipline has proven to allow sites to avoid the cost and time associated with the temporary burners. Even without a pilot ignitor designed for large heat input to the thermal reactor, keeping thermal reactor heating rates within the API recommendation has repeatedly been demonstrated with the practice of “pulse firing.”

In pulse firing, the operators will fire the thermal reactor burner for very short durations in the early stages of heatup with time in between each pulse to allow thermal reactor temperature to decrease or hold. Keeping an average (not an instantaneous or minute-by-minute) heating rate of <200°F/hr, as measured by thermal reactor temperature indication devices that measure hot face temperature, will allow for adequate heating through the bulk of the refractory lining system to avoid damage from rapid thermal expansion.

Some pulse firing data are shown below as examples of successfully controlled heating rates, even through the very low range, with direct ignition of the main burner in the thermal reactor for refractory dry-out and refractory heatup. The pulse pattern will depend largely on the thermal reactor configuration, burner design, turndown ability, and any BMS/SIS limitations on minimum firing (i.e. flow trip points, supply pressure trip points, flame scanner tuning/stability, etc). Some will require longer-duration pulses spaced further apart to achieve a target average heatup rate as shown in Figure 1 below. In this case, the burner is not well-sized for the low firing rate and instrumentation limits the turndown ability for the control system. As such, the instantaneous heating rates do get quite high, but the longer-term average heatup of the bulk refractory is viewed as manageable to avoid refractory damage.

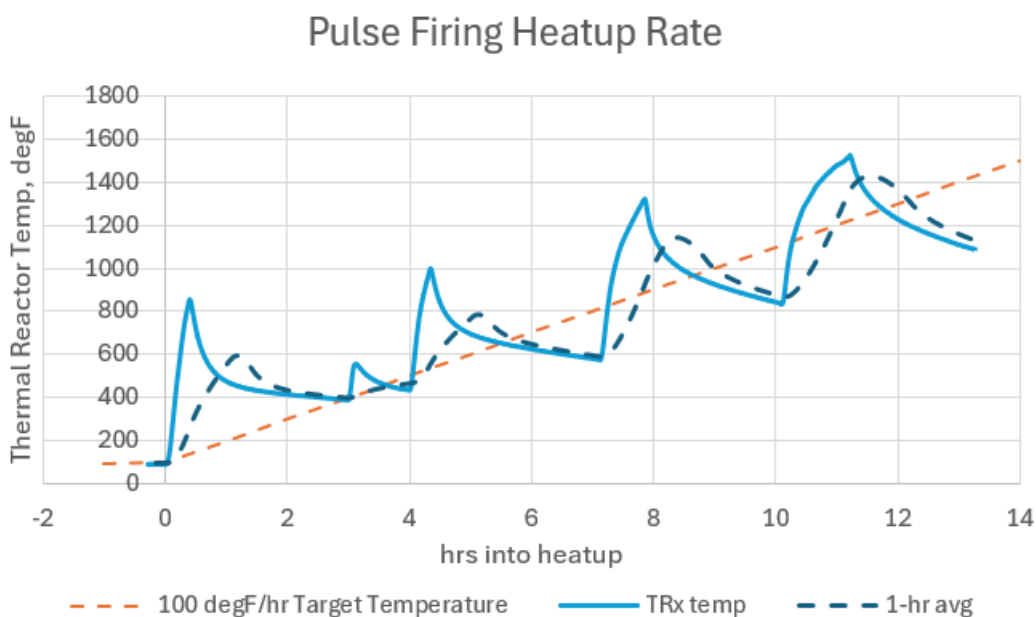


Figure 1: Pulse firing with large open-pipe burner, limited turndown

However, some with better burner design/sizing for turndown and a reliable BMS/ignition system can pulse fire the thermal reactor in shorter durations much more frequently as indicated below. Figure 2 below shows actual thermal reactor temperature followed by the rate-of-change for both thermal reactor and WHB heatup rates. Note the multiple short-duration pulses at the beginning then continuous firing achieves well under the recommended heating rates on a 1-hr average basis.

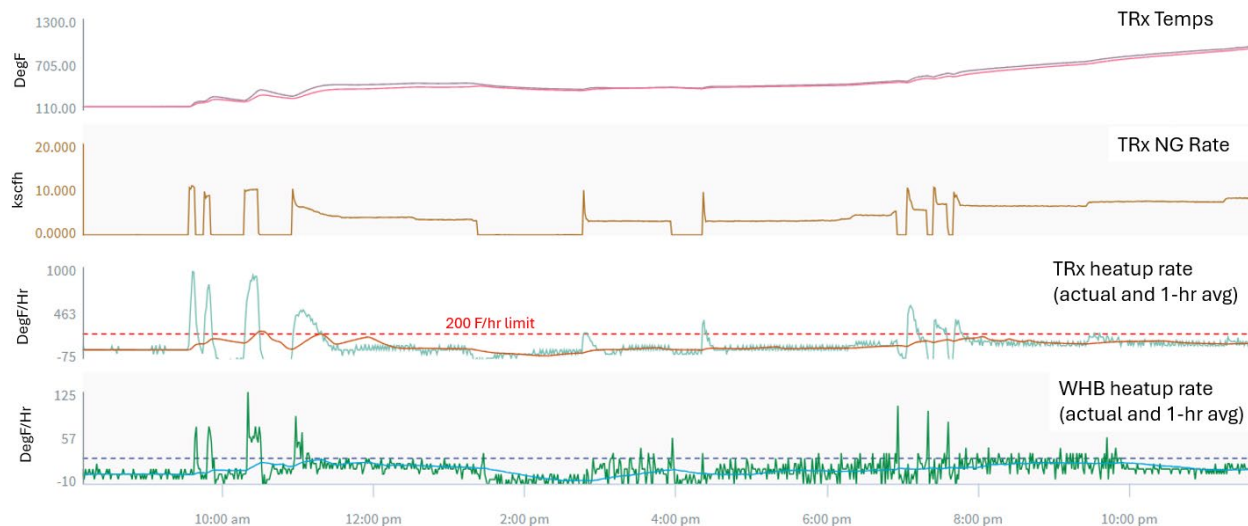


Figure 2: Pulse firing example – very good turndown ability, good BMS/SIS configuration

Inspection results for many thermal reactors throughout the company during planned turnarounds, where this pulse firing heatup procedure is regularly practiced, confirm that no significant damage has regularly been observed despite the short bursts of rapid temperature rise at the hot face temperature measurement.

Minimum Converter Bed Temperature

The rationale for long-standing guidance to establish minimum converter bed temperatures prior to tempering steam or acid gas feed introduction is likely due to several factors. One of those is the desire to avoid water condensation within the beds from tempering steam injection while firing natural gas (NG) for heat-up. As the usual thermal reactor operation while heating up and preparing for acid gas introduces the potential to exceed thermal reactor refractory temperature limits from natural gas combustion capable of reaching ~3500°F or higher, introduction of tempering steam is a common practice for mitigation of that concern. Typical guidance suggests injecting tempering steam on a mass ratio with the fuel rate, usually in the range of 2:1 to 4:1 lbs steam to lbs fuel.

Following past procedural guidance requiring that the converter beds be heated up to a minimum temperature of 250°F prior to introducing tempering steam introduces the possible inability to inject tempering steam as soon as needed for thermal reactor temperature management or soot avoidance. The basis of delaying tempering steam injection, however, possibly overlooked the fact that there is already substantial water vapor content in the combustion flue gas going to the converter beds. In fact, the water vapor concentration in the flue gas with no tempering steam ranges from 12 – 20%, depending on excess air according to Figure 3 below, over an expected excess O₂ range

during heatup from 0.5 (@ 10:1 air/NG ratio) to well over 10% O₂ (@ 20:1 air/NG). With the higher tempering steam ratios, the H₂O content on a mol% basis can increase notably; however, the actual impact on water dewpoint of the steam is relatively small. Figure 3 shows the range of water dewpoint values over this same range of air/NG ratios and a typical range of tempering steam is anywhere from ~125 - 175°F depending on air/NG ratio and tempering steam rate.

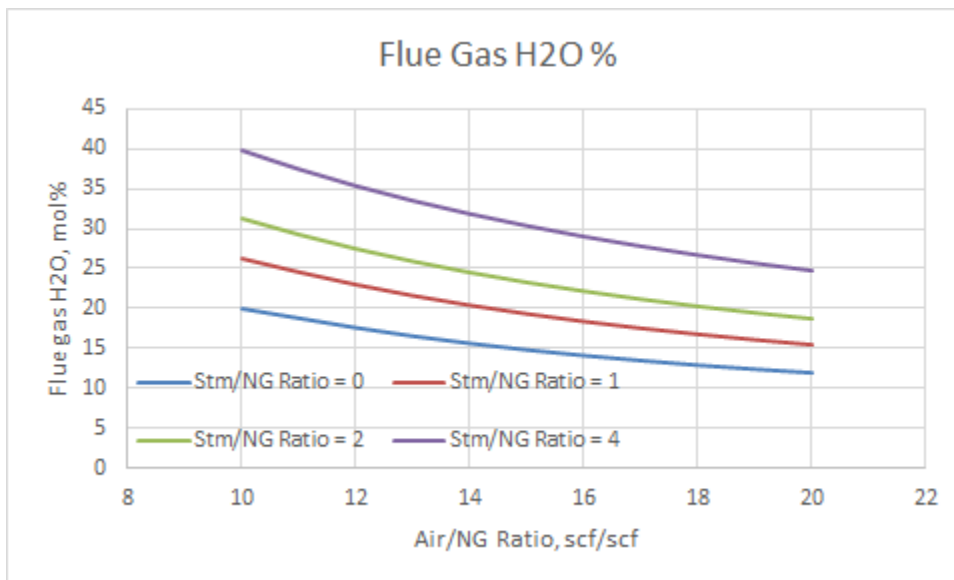


Figure 3: Flue gas H₂O content as a function of air/NG ratio

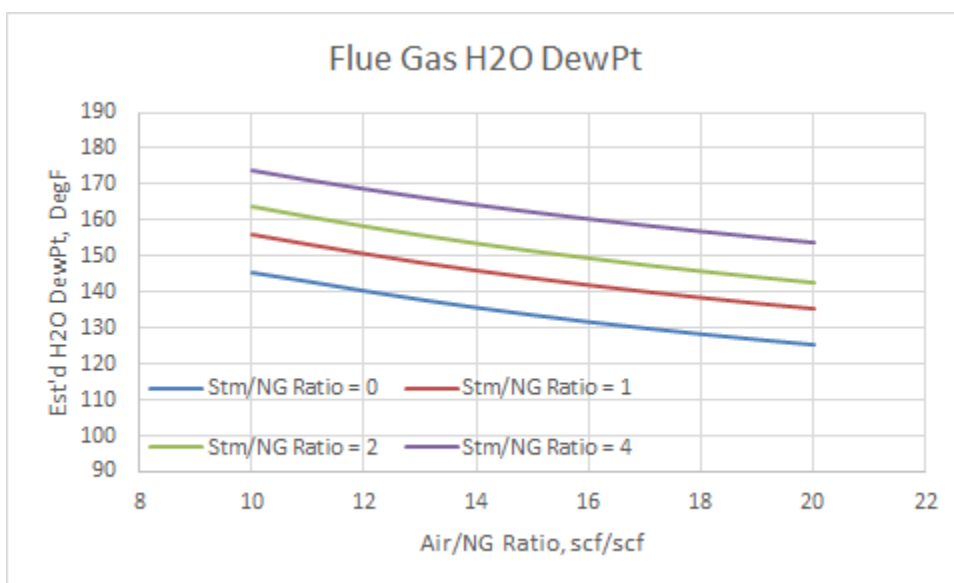


Figure 4: Flue gas water dewpoint as a function of thermal reactor air/NG ratio and tempering steam injection rate

Experience across the sites in most startups is that with the heat from combustion air blowers, and sometimes with heat from charging condenser levels with hot boiler feed water, the converters are usually above expected dewpoint, with or without the addition of tempering steam, by the time the thermal reactor is lit. With this consideration, any precautionary steps to wait for bed temperatures to $>250^{\circ}\text{F}$ prior to tempering steam introduction is ultra conservative. Proceeding with steam injection earlier in the startup procedure allows for more proactive measures to avoid soot formation if firing near stoichiometric ratio and avoids exposing refractory and burner metal components to temperatures that might result in equipment damage.

The other, and historically more widespread, concern with cool converter bed temperatures has been condensation and possible freezing of sulfur once acid gas feed is introduced. With introduction of acid gas feed, elemental sulfur will be created via the Claus reaction that has the potential to condense on any cooler areas of the converter bed. That would have the potential to reduce overall sulfur conversion or, in more extreme cases, result in higher dP through the converter bed. The conventional guidance for minimum converter temperature required for acid gas introduction ranges from $\sim 300^{\circ}\text{F}$ up to 400°F .

Experience has shown that SRU startups can proceed reliably from a cold converter state without detrimental effects from sulfur condensation. Aside from successful company operating experience at multiple sites, Ortloff has published information as long ago as 1998 advertising the benefits of a “Cold Reactor Bed Startup” with their demonstrated success going back into the 1970s [1].

The charts below illustrate observed converter bed temperatures in a startup for an SRU that routinely introduces acid gas prior to lighting the direct fired reheaters since available fuel is a refinery gas stream with widely varying concentration. Of particular interest is the sharp rise in the top bed temperature indications, especially in the first bed where more conversion takes place. The time between the introduction of acid gas and lighting each of the reheaters is about 5 hrs. Although not explicitly shown in the data for this or other startups of this SRU, plugging from sulfur condensation has not been observed with feed introduced at the relatively cold converter bed temperatures.

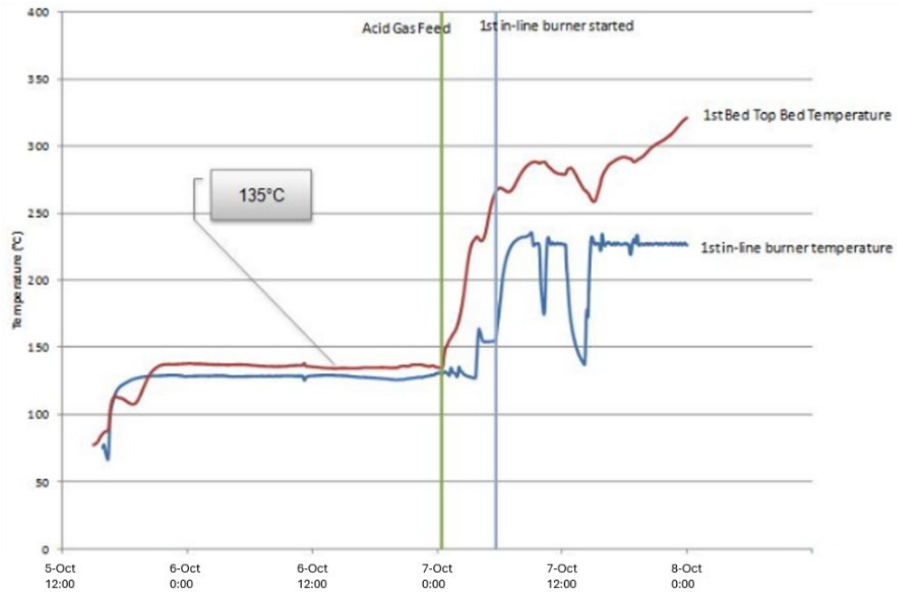


Figure 5: SRU cold bed s/u – first bed temperatures

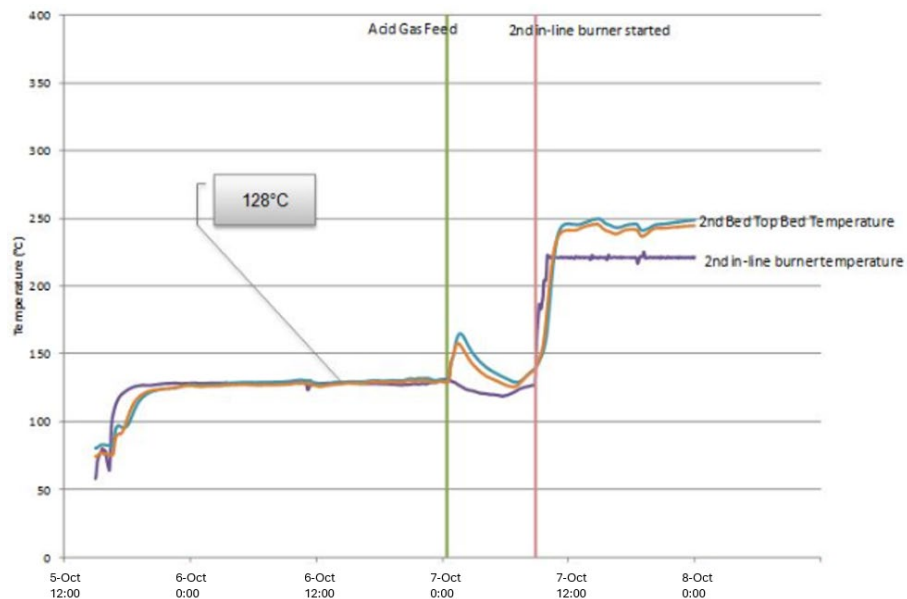


Figure 6: SRU cold bed s/u – second bed temperatures

It should be noted that the SRUs referenced in the company experience here are not designed with a bypass around the Claus converters. Subsequently, thermal reactor gases were flowing through the reactor beds before acid gas feed introduction. While it's possible that some sulfation of the catalyst could occur in a startup with used catalyst in this configuration, experience has shown the practical impact to be negligible or recoverable with an online rejuvenation procedure.

There are a number of circumstances where this procedure might be advantageous in avoiding damage or shortening the startup duration, thus reducing total emissions. Of particular interest would be an SRU, as shown in the figures just above, with fired reheaters but very unreliable fuel composition for startup rather than a more stable natural gas supply. Minimizing or eliminating the time in operation with the fired reheaters to avoid possible soot formation from improperly controlled stoichiometry might make a startup from cold converters particularly appealing. Other circumstances to necessitate the cold startup might include an SRU with poorly designed or damaged reheater burners that might soot or allow excess oxygen slip (or both!) due to improper mixing of air and fuel. Accumulation of sooting at the top of the converter could lead to a flow restriction, resulting in reduced SRU capacity, while excess O_2 could lead to several more immediate consequences.

Of utmost concern, especially in the case of an SRU that might not have completed a full shutdown as described earlier in the paper, is exposure of pyrophoric material in the converter or downstream equipment to oxygen. This would lead to oxidation reaction exotherms, sometimes severe, with the added possibility of igniting sulfur remaining in the equipment, thus leading to equipment damage and increased SO_2 emissions during startup. In that case, a cold bed startup procedure allowing transition directly to acid gas immediately upon lighting the fired reheater would both avoid soot formation and limit oxygen exposure to the possible pyrophoric material that could ignite remaining sulfur from the dirty shutdown.

Sulfiding Tail Gas Catalyst

After the SRU startup and preparation steps, attention turns to the TGTU. Most modern TGTUs use a hydrogenation reactor filled with a cobalt/molybdenum (CoMo) catalyst either on an alumina or titania base. The purpose of this reactor is to convert all residual sulfur species in the SRU tail gas (SO_2 , S_x vapor, COS, CS_2) into H_2S by hydrogenation/hydrolysis so that H_2S can then be removed (usually by amine scrubbing) and recycled. Before this CoMo catalyst can do its job, it must be activated by converting it from metal oxide form to metal sulfide form, or “sulfiding.” This is a common requirement for all hydrotreating catalysts (CoMo or NiMo) which are shipped in oxidized state to eliminate risks with handling pre-sulfided catalyst that is pyrophoric and could react with O_2 in ambient air conditions to generate exothermic activity and release SO_2 .

Many licensors’ SRU/TGTU designs and catalyst vendors’ startup procedures have historically included a sulfiding procedure which involves using a dedicated H_2S source directly to the hydrogenation reactor inlet for in-situ sulfiding of the hydrogenation catalyst. A common source for this sulfiding gas is a slip stream of the amine acid gas feed stream,

before introduction of feed to the SRU, that bypasses all or most of the SRU. A recent ASRL paper from 2023 Brimstone Sulfur Symposium has shared experimental data that confirms past company operating experience that sulfiding with tail gas from the SRU can be effective, under the right conditions, and lead to adequate conversion activity in the TGTU. The ASRL paper compared sulfiding with a conventional sulfiding gas containing 2.5% H₂S and 10% H₂ (remainder N₂) to a typical tail gas stream with 1.2% H₂S, 0.4% SO₂, 8% CO, 1.7% H₂, 30% H₂O and other typical constituents (CO, COS, CS₂, N₂). The study concluded that “While the conventional method led to more active catalysts in both cases, depending on the conditions, sulfiding with a Claus tail gas itself may lead to sufficient reactivity” [2]. It should be noted that the operational experience noted above is from refinery SRUs with fairly steady and ideal feed conditions that may not warrant robust or maximum extents of catalyst sulfiding. It has been observed that the activity achieved from sulfiding with tail gas has allowed the TGTUs to operate below required emission levels between turnarounds. The recommendation remains to discuss any deviations from the suppliers’ in-situ sulfiding procedures while adapting to new or novel procedures.

Using the SRU tail gas as the sulfiding agent conveniently provides an on-site and readily available source of H₂S for sulfiding once the SRU is up and running on acid gas. The tail gas from the Claus unit contains H₂S and H₂ (as well as some SO₂ and other sulfur compounds). With H₂, which already is present in the tail gas stream but can be supplemented from a make-up hydrogen line or an in-line NG-fired reducing gas generator (RGG), and H₂S present, the CoMo catalyst will begin to convert from MoO₃ to MoS₂ and CoO to CoS as the sulfiding reactions proceed.

The concerns and risks with catalyst sulfiding are mostly identical whether tail gas or a specific H₂S source direct to the TGTU is used as sulfiding agent. The presence of H₂S is critical because both cobalt and molybdenum oxides need H₂S to transform – cobalt oxide converts to cobalt sulfide directly ($\text{CoO} + \text{H}_2\text{S} \rightarrow \text{CoS} + \text{H}_2\text{O}$), and molybdenum oxide needs H₂S plus H₂ to reduce the valence of the Mo to MoS₂ ($\text{MoO}_3 + 2\text{H}_2\text{S} + \text{H}_2 \rightarrow \text{MoS}_2 + 3\text{H}_2\text{O}$).

Never introduce hydrogen without H₂S into a hot reactor above ~390°F (200°C), as that can permanently reduce the metal oxides to elemental cobalt/molybdenum, a form which then will not sulfide properly. Thus, ensuring a healthy H₂S level in tail gas is key. Control of the H₂S composition, in practice, is easily achieved with tail gas sulfiding if the SRU is running properly and achieving >0.5% H₂S is not difficult.

Exposure of the hydrogenation catalyst and reactor equipment/piping to excessive temperature is also a concern regardless of sulfiding method. The sulfiding reactions are exothermic – as H₂S reacts with the oxides, the bed temperature will rise (a “temperature wave” moving through the catalyst). Operators monitor the bed temperatures closely via

thermocouples placed at multiple levels in the reactor. The rate of introducing H_2S in the tail gas can be adjusted to control the temperature rise so that it isn't excessive. Typical procedures will target a moderate inlet temperature, usually 400–500°F, during sulfiding to allow for exotherms without damaging catalyst or equipment before eventually ramping up to the target ~600°F “high temperature soak” range. If temperature starts to run away, one can reduce H_2S by adjusting thermal reactor air/acid gas ratio to limit the dT from sulfiding reactions.

A distinct advantage of utilizing tail gas for sulfiding is a shorter overall startup duration due to better management of the sulfiding exotherms. The traditional acid gas slip stream sulfiding method requires thermal reactor firing near stoichiometric air/fuel ratio for SRUs that cannot bypass the TGTU and therefore have tail gas flowing through the hydrogenation reactor. Thermal reactor excess oxygen control and temperature management (even with tempering steam) can become difficult and often limit the total flow rate through the SRU/TGTU. The relatively low flow rate required to not exceed refractory limitations is only a moderate heat sink for the sulfiding exotherms, so the rate at which sulfiding gas can be introduced is often limited. Since sulfiding can't adequately take place with oxygen in the stream, the thermal reactor (and fired reheaters) must be operated at near-stoichiometric ratio. Aside from the temperature concerns associated with firing without excess O_2 , this introduces the risk of soot formation for the duration of sulfiding.

Another concern with the low thermal reactor flow rate in conventional sulfiding is that the rate-limited (or possibly bypassed) tail gas stream leaves the RGG mixing chamber vulnerable to overheating and possible high-temperature trips during sulfiding. Historically, this has led to TGTU designers to include additional equipment such as steam-driven recycle ejectors or recycle blowers which only intermittently operate for startups, sometimes separated by years of being idle with the possibility of sour/sulfur-laden process stream intrusion causing corrosion and plugging. The blowers, especially, almost always turn into a high-cost maintenance item leading to startup delays. Sulfiding with tail gas allows for higher tail gas rate through the RGG that will not only improve the sulfiding process but, if considered in the design phase, could reduce total cost of the TGTU.

By using tail gas for sulfiding, the SRU can move directly from operating with excess oxygen in the thermal reactor to burning acid gas. This avoids an extended transition period where refractory could overheat or soot could form and plug equipment. In addition, the convenience of introducing acid gas and combustion air at a much higher flow rate through the SRU and TGTU, since acid gas and combustion air will be near normal operating ratio and thermal reactor temperature, is possible while staying in a normal temperature range far below the ~3000F refractory limitation. This higher tail gas flow rate acts as a more

effective heat sink that lessens the magnitude of hydrogenation reactor exotherms and helps push the temperature wave through the reactor bed more quickly. The limited magnitude and faster passing of exotherm waves has proven to shorten the time required for the overall sulfiding procedure.

Adjustment of the H₂S content, if needed for exothermic temperature control, is still easily done with air/acid gas ratio changes at the thermal reactor. Experience shows that H₂S concentration, as conveniently measured with the in-service air demand analyzer, is easily controllable within a range of 0.5% to even higher than 2% H₂S as exothermic activity allows.

The tail gas sulfiding method is convenient – it uses the plant’s own H₂S stream rather than requiring an external acid gas slip stream or presulfided catalyst. Tail gas sulfiding ensures the catalyst sees the actual process gas composition it will handle, making the activation more controlled. Additionally, this approach does not require handling any chemicals other than those already present in the unit. When adequate H₂S is present, oxygen is absent, and the temperature ramp is properly managed, sulfiding with tail gas proceeds efficiently and typically completes in less time than the slip stream sulfiding method. With the TGTU fully operational, the sulfided catalyst can confidently achieve high conversion and long operating duration.

Summary

Achieving faster SRU/TGTU startups while maintaining regulatory emissions limits and ensuring reliable operation is possible with adoption of industry experiences and development of best practices to establish procedural expectations for safe startups. A few of the historical status quo items that have proven to reveal opportunities for improvement are summarized as follows:

- Employing the practice of pulse firing the thermal reactor can save time and money during the turnaround by eliminating the need to bring in a portable burner specifically for dryout and heatup through the low-temperature range. Additionally, it can help to ensure heatup rates doesn’t exceed recommended limits for thermal reactor refractory lining components (<200 °F/hr) as well as the WHB (<25 °F/hr).
- Focusing on an average heatup rate is appropriate where the thermal reactor temperature measurement device only gives hot face temperature.
- Don’t wait on Claus reactor bed temperatures before introducing tempering steam to the thermal reactor. Delaying tempering steam can lead to soot formation that could limit SRU throughput capacity or allow for high temperature that damages refractory. While many startups occur with clean downstream SRU equipment that

has been adequately passivated and sulfur-freed during the shutdown steps, some situations might require near-stoichiometric air/NG combustion immediately at startup with the ability to inject tempering steam being mandatory for proper thermal reactor temperature control

- Acid gas can be introduced with reactor bed temperatures much colder than most licensors would originally have allowed. With very large reactor beds, for example, experience has shown that waiting on minimum temperatures to exceed even 250°F could lead to additional shifts or days before acid gas feed is introduced. Additionally, this flexibility can decrease the time required to operate with poorly designed or compromised fired reheater equipment, thereby minimizing the risk of sooting or exposing downstream catalysts and equipment to oxygen. This is achieved because fired reheaters may be brought online immediately prior to feed introduction, rather than significantly earlier solely to attain minimum bed temperatures.
- The use of tail gas sulfiding can save time and mitigate SRU front-end concerns related to soot formation and high temperature when at near-stoichiometric firing conditions while Operations focuses on the sulfiding activity in the TGTU reactor. Higher achievable throughput during the process limits the magnitude of expected exotherms and pushes the “temperature wave” through the bed, effectively shortening the duration of the sulfiding procedure with a large portion of acid gas feed introduction having occurred at the beginning rather than after all sulfiding steps have been completed.

References:

[1] Hudson H. and Grigson, S; “Alternative Design Concepts to Improve Sulfur Facility Reliability”; Brimstone Sulfur Symposium, September 1998.

[2] Lavery, C, Ruohong, S, Jacobs J H, Deering, C E, Li, D, and Marriott R; “Titania and Alumina Supported Co-Mo Catalysts for Hydrogenation of Sulfur Compounds: A Morphology and Reactivity Study”; Brimstone Sulfur Symposium, September 2023.

[3] API Std 565; section d.4.4